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Behaviour of CaO coating of gas atomized Mg powders using mechanical milling process

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ABSTRACT

In order to synthesize a thermally stable Mg powder as a desulfurizer of iron, pure Mg was gas atomized to powders and coated by CaO powders, to produce a thermally stable desulfurizer using a mechanical milling process. Since the effect of desulfurization is dependent on the degree of surface modification, coating behaviours such as the size, morphology and layer thickness were investigated as a function of milling condition. As the milling conducted from 10 min to 30 min, 1 h, 3 h, 6 h, 12 h, CaO particles began to stick on the surface of Mg powders. The layer of CaO formed from 1 h milling was about 17 μm thick and gradually thickened to be 28 μm, 32 μm and 37 μm with increasing the milling time to 3 h, 6 h and 12 h, respectively. The shape of coated powder became more spherical after 1 h milling, being mostly spherical after 6 h. Desulfurization rate and uniformity were evaluated for the various thickness of the coating layer.

1. Introduction

Mg is widely used in various areas such as aerospace and automobile industries, due to low density and high specific strength, but also iron and steel making industries due to its strong desulfurization effect [1,2]. Among the industrial uses, desulfurization accounts for about 20% worldwide, and is increasing due to an increase of demand for high quality steel production.

Compared with other conventional agent, Mg is generally known to bear the about 10 times high desulfurization rate (about 0.084–0.306 min^{-1}) as well as 4–8 times low slag emission [3]. Nevertheless, fabrication of Mg desulfurizer is limited due to the easy flammability characteristics. Although several alternatives have been developed such as Mag-Coke, Soalt-coated magnesium, cored wire and Mg-Lime methods, and Co-injection methods, more effective production technology of Mg powder is highly desirable [2–4]. Among the powder processes proposed, a pulverization process which is most frequently used with magnesium scrap reported to induce not only an incorporation of the impurities, but also a frequent fire and explosion during the powder preparation [2,4]. Thus, production of uniformly sized Mg powders while preventing explosion became the primary focus. The gas atomization process is a strong alternative for the synthesis Mg powders as a desulfurizer, since it is known to be useful to produce the powder type materials with a relatively uniform shape near to spherical as well as uniform composition and size distribution. In addition, modification of atomized Mg powder surfaces can be easily conducted using the milling process, since the powder surfaces are very even in roughness, shape and purity [5].

In this study, Mg powders are prepared by using the gas atomization process and coated with CaO using the mechanical milling method. CaO also bears the desulfurization effect with more stability in elevated temperature. Microstructure and morphology of gas atomized magnesium powders and behaviour of CaO coating were examined by scanning electron microscope (SEM). Desulfurization effect of CaO coated Mg powders was evaluated in electrolytic iron.

2. Experimental procedure

Mg powders were fabricated using a high pressure gas atomizer with a silicon nitride melt delivery nozzle of 5 mm in diameter and an annular Ar gas nozzle. Fig. 1 is a schematic diagram of a vertical inert gas atomizer that consists of electric furnace, melt delivery nozzle and atomizing chamber (cyclone). The melt was prepared by induction heating to a temperature 200 °C over the liquidus prior to entering the melt nozzle. The melt flow rate, as estimated from operating time and weight of atomized melt was about 1.0 kg/min, while the gas pressure was about 2 MPa. The average size distribution of gas atomized alloy Mg powders was about 250 μm in diameter. In order to coat the CaO particles on the gas atomized Mg powders, CaO powders with less than 2 μm in particle diameter was selected, and put in stainless steel jar of high energy planetary mill (Fretch Pulverisette-5, Germany) with Zirconia balls. Mass ratio between the Mg and CaO powders for milling was 9:1, while the mass ratio between the total powders and ball was 20:1. Zirconia ball used for the experiment was about 5 mm in diameter.

Milling was conducted at 300 rpm for 10 min, 30 min, 1 h, 3 h, 6 h and 12 h under Ar atmosphere. Microstructure and thickness variation with the milling condition

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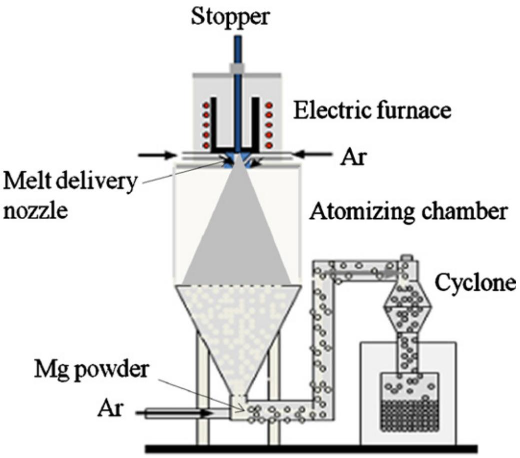

Fig. 1. A schematic diagram of gas atomization apparatus.

were observed using scanning electron microscope (SEM, JEOL), and the compositional change analyzed using EDS (Oxford) on the SEM.

In order to investigate the desulfurization effect of CaO coated Mg powders with the coating thickness, a desulfurization experiment was carried out on electrolytic iron at 1750 °C using a high frequency induction furnace [6]. The desulfurization reaction was conducted for 5 min. The amount of sulfur was analyzed using inductively coupled plasma (GDC Intergra Xmp 2).

3. Experimental results and discussion

Gas atomized Mg powders were nearly spherical with an average size of near 250 μm, whereas the CaO powders of near 2.0 μm in diameter presented a rather irregular morphology. Fig. 2 shows the morphology change of Mg powders and CaO powders with milling as determined by SEM. It is seen that the Mg powders became spherical as the milling time increased from 10 min (a) to 12 (f). During the very initial milling for 10 min (a), no reaction was found to occur, determined from the separate existence of both powders with the no change in morphology. Milling for 30 min (b) and 1 h (c) resulted in increasing the roundness of powders. The powders showed the highest degree of roundness and homogeneity in size after 3 h (d) and 6 h (e), followed by losing the roundness by further milling for 12 h (f). In order to examine the milling behaviour of

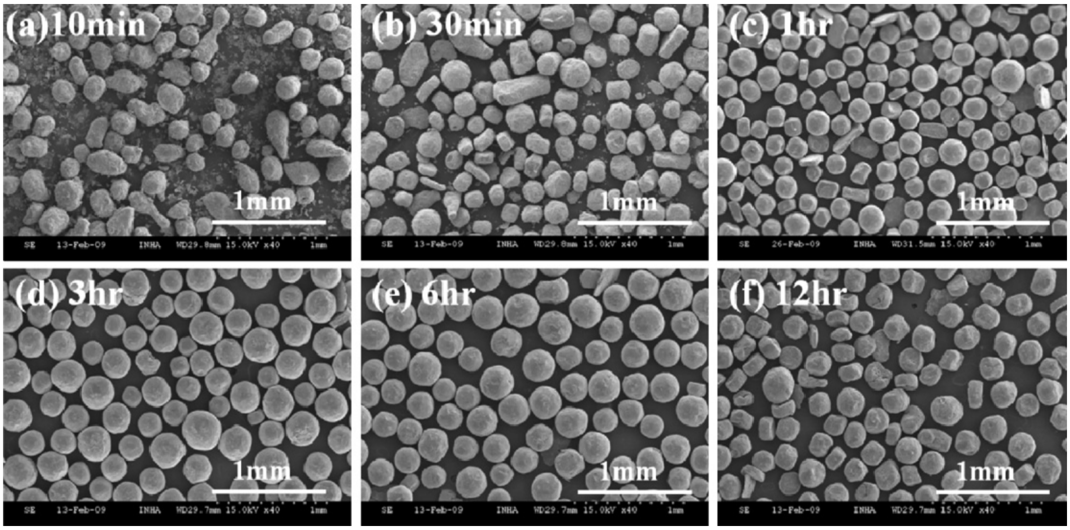

Fig. 2. SEM images of CaO–Mg powders, showing the effects of various milling times on the morphology of the powders.

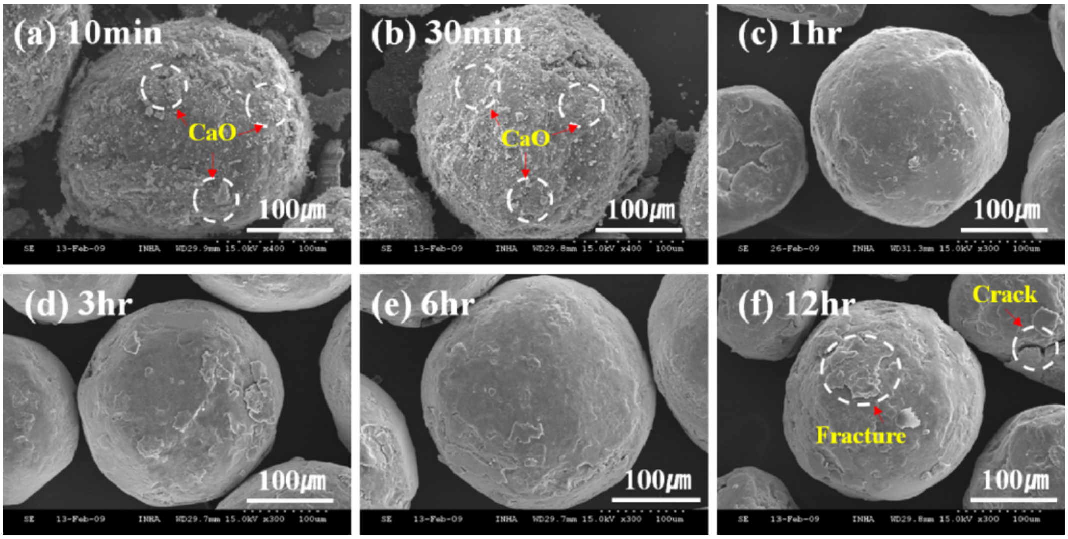

Fig. 3. Magnified SEM image of coated Mg powders shown in Fig. 2.

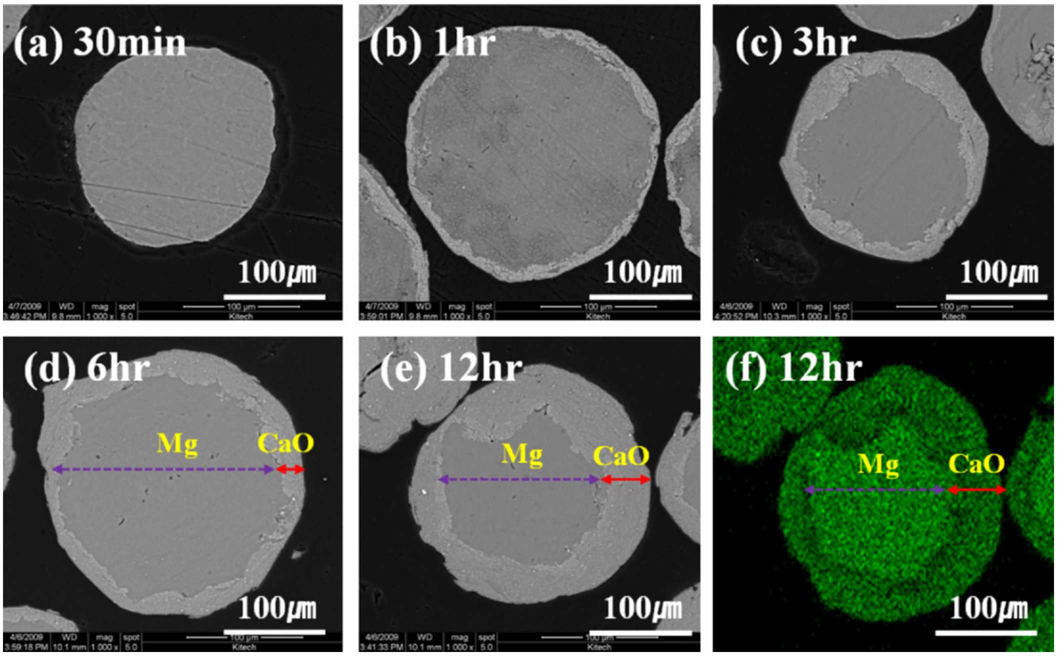

Fig. 4. SEM microstructure and EDS map of CaO coated Mg powders in cross section.

both the Mg and CaO powders in detail, the surface of powders were observed by SEM as shown in Fig. 3. It is seen that the fine and hard CaO powders begun to stick on the coarse and soft Mg powders until 30 min (b), and were incorporated to inside the Mg powders until 6 h (e) with some fracturing by further milling for 12 h (f) [7]. The reaction behaviour with milling time changed the surface roughness as well as the resultant size. Due to sticking and incorporating of hard and fine CaO powders on the coarse and soft Mg powders continually induced an increase (Fig. 3a and b) and decrease (c and d) in the size of milled powder. On the other hand, during milling to 6 h the size became increase again possibly due to attachment of the other reacted Mg–CaO layers. After milling for 12 h, the size became small due to fracturing possibly by the concentration of milling impaction. Similar behaviour was also reported elsewhere [8].

Fig. 4 shows the variation of coated layer in thickness and composition detected using SEM/EDS mapping technology. The CaO layer began to form on the surface of large Mg powder particles after milling for 1 h. The thickness of the CaO layer gradually increased from about 17 μm at 1 h to 28 μm for 3 h, 32 μm for 6 h and 37 μm for 12 h.

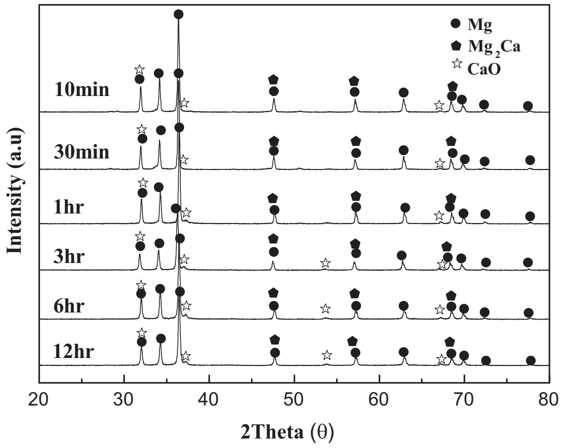

Fig. 5. X-ray traces of CaO coated Mg powders.

Table 1
Comparison of thermal stability of pure Mg and CaO coated Mg powder in electrolytic iron.

Desulfurizer type	Initial of sulfur: 0.013%
Pure Mg	0.009% (burning)
CaO coated Mg (6 h)	0.004% (stable injection)

Fig. 5 shows the XRD traces of CaO coated Mg powders for various times of milling, indicating no formation of new reaction phase with the milling, only the input elements of Mg and CaO.

Table 1 shows the results of the desulfurization experiment, comparing the stability of Mg and CaO coated Mg against the iron melt, in which the coated Mg showed better desulfurization as 0.004% S remained rather than the pure Mg (0.09% S). This may be due to the easy and rapid evaporation of pure Mg, whereas the CaO layer prevented this reaction of Mg. The variation in sulfur content with the coated layer thickness is listed in Table 2, in which the sample was commonly extracted from the central part. Degree of desulfurization was increased from the remained sulfur value of 0.009% to 0.004% as the milling time increased (coated layer thickness increased) from 10 and 30 min to 6 and 12 h. The same sulfur contents of 10 and 30 min milled sample (Table 2) with the non-milled sample (Table 1) was possibly due to no formation of CaO layer at the milling condition (Fig. 4). The small change in desulfurization after 1 h milling may correspond to the fact that the 28 μm CaO layer formed after 1 h became a critical thickness for retarding the reaction between the Mg and iron melt. Further increase in

Table 2
Sulfur content in electrolytic iron for various milling times/coated layer thickness.

Milling time	Initial of sulfur: 0.013%
10 min	0.009
30 min	0.009
1 h	0.005
3 h	0.005
6 h	0.004
12 h	0.004

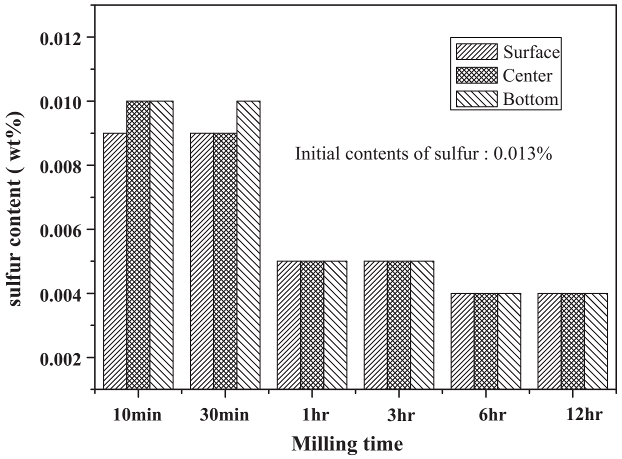

Fig. 6. The variation of sulfur content with milling time and iron melt position.

the thickness did not affect to improve the protection. Also, small change in the mass of Mg did not lead to further desulfurization. Fig. 6 shows the degree of desulfurization of iron depending on the position (surface–center–bottom part) of specimen as a function of thickness of CaO layer (milling time). During the initial milling time of 10 and 30 min, the contents of sulfur was not remained uniform with the position, where the content was low in the surface area. This was attributed to the direct reaction between Mg and iron due to no formation of thermally stable CaO layer. However, the S content became uniform at the iron reacted with CaO coated Mg for 1 h. Thus, the existence of CaO layer would protect the direct contact between Mg and surface part of iron melt, so that the CaO–Mg powders could move to the central and bottom part, resulting in the uniform desulfurization.

4. Conclusions

CaO coated Mg powders, which can be used for sulfur removal, were successfully prepared using a combination of gas atomization and mechanical milling processes. The gas atomized Mg powders were spherical in shape and had an average diameter of about 250 μm. Milling the Mg powders with CaO powders for 1 h began to produce CaO layer (17 μm thick) on the surface of Mg powders, and the thickness was increased to 28 μm, 32 μm and 37 μm as the milling time increased to 3 h, 6 h and 12 h, respectively. CaO coating for 1 h or more resulted in maximized degree and homogeneity of desulfurization.

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