

Effect of CaO composition on oxidation and burning behaviors of AM50 Mg alloy

Jin-Kyu LEE, Shae K. KIM

Advanced Material Division, Korea Institute of Industrial Technology,
7-47 Songdo-Dong, Yeonsu-Gu, Incheon 406-840, Korea

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Abstract: Oxidation and burning behaviors were studied for CaO added AM50 Mg composites which were manufactured by conventional melting and casting processes without SF₆ protective gas. CaO added AM50 Mg composites show the stable oxidation resistance, while AM50 Mg alloys show the poor oxidation resistance. The effects of CaO addition on the burning resistance under ambient, nitrogen and dry air atmospheres were examined for CaO added AM50 Mg composites. With increasing CaO addition, the burning temperature increases under ambient, nitrogen and dry air atmospheres. The burning temperatures of small test specimen under all conditions greatly increase even by 0.3% CaO (mass fraction) addition into AM50 Mg alloys.

Key words: Mg alloy; CaO; oxidation behavior; burning behavior

1 Introduction

AM50 Mg alloy has already been applied to certain automobile parts, such as instrument panel, seat frame, air-back housing, sub-frame, valve cover, steering wheel and steering column parts[1–5]. However, Mg alloys are easily oxidized and rapidly burn when they are exposed to high temperature or fire by accident[6]. Oxidation and burning retardation solution for Mg products has been studied by developing new Mg alloys. It is well known that Be and Ca are used to improve the oxidation and burning resistance of Mg alloys[7–11]. Be addition in Mg alloys can also improve the oxidation resistance of Mg alloys. The burning of the alloys, however, cannot be prevented completely and high Be concentration will deteriorate the mechanical properties. Generally, the allowed maximum mass fractions of Be in Mg alloy are 0.01% for permanent mold casting and 0.002% for sand mold casting[8]. Be addition should be also carefully handled because of its toxicity. The oxidation of Mg-Ca alloys was studied by SAKAMOTO and AKIYAMA[12]. The results showed that the burning resistance could be increased by 423 °C after 5% Ca was added. However, Ca is expensive and difficult to handle due to its high reactivity under an ambient atmosphere. More than that, Ca decreases fluidity and increases hot tearing

susceptibility during casting processes. CaO added Mg composites have also been developed to improve oxidation and burning resistances of Mg alloys[13–18], like Ca addition in Mg alloy. CaO is cheaper than Ca and easy to handle due to its stability. CaO addition to Mg alloys forms the Al₂Ca phase without solid solution regardless of CaO composition, that is, even at 0.05% CaO addition.

This work discussed the results of the oxidation and burning behaviors for CaO added Mg-based AM50 Mg alloy. The CaO added AM50 Mg composites were manufactured by conventional melting and casting procedures under ambient atmosphere without any protective gases. The effects of CaO on the oxidation and burning resistances under ambient, nitrogen and dry air atmospheres were examined for CaO added AM50 Mg composites.

2 Experimental

AM50 Mg alloy was melted in a steel crucible in an electric resistance furnace at 730 °C in SF₆ and CO₂ gases. The CaO with desired mass fraction was added into molten AM50 Mg alloy. After the CaO addition, the protective gas was no longer used. The CaO added melts were then cast into steel mold preheated at 100 °C without SF₆ protective gas. The chemical compositions

were determined by ICP-mass spectrometer. In order to observe the microstructure change by CaO addition, the cast billets were polished and observed using an Olympus PME3 microscope. Oxidation test was performed with thermogravimetric analyzer (TGA, TA Q600) to investigate the effect of CaO on oxidation resistance of AM50 Mg composites. TGA was performed at 500 °C for 7 h. After TGA, the surface was analyzed by AES (Auger Electron Spectroscopy). The chips were prepared from CaO added AM50 billets using a drilling machine without cutting oil for burning test under an ambient atmosphere. The machined chips on a steel boat were put in an electric resistance furnace at 700 °C under an ambient atmosphere. Temperature change of the chips was investigated by a thermocouple inserted into the chips. The burning temperatures were detected when the burning occurred, and based on the average of 10 tests. Differential thermal analysis (DTA) was performed to investigate the effect of CaO on the increase of burning temperature under nitrogen atmosphere as well as to evaluate the possibility for applying nitrogen gas as a melt protective gas. The sample mass for the burning test under nitrogen atmosphere was 20–30 mg. The burning temperatures under nitrogen atmosphere were detected by abrupt temperature increase and based on the average of 3 tests. Burning resistance in dry air was also performed. The sample mass for the burning test in dry air atmosphere was 1–3 mg. The burning temperatures under dry air atmosphere were detected by abrupt temperature increase and based on the average of 3 tests.

3 Results and discussion

3.1 Casting of CaO added AM50 Mg composites

In Fig.1, the surfaces of AM50 Mg alloy and 0.27%

CaO added AM50 Mg composite during casting and solidification are shown. Fig.1(a) shows the surfaces of AM50 Mg alloy during casting under an ambient atmosphere without SF₆ protective gas. Oxidation occurred just after pouring for 10 s, and tarnished surface appeared. Burning rose on the surface is shown in Fig.1(b). After 40 s (Fig.1(b)), burning oxides on the surface of AM50 Mg alloy increased. Figure 1(c) shows the surface of AM50 Mg alloy after solidification. The surface shows flame and burning pit. The burning of AM50 Mg alloy in the molten state occurred because of the porous surface MgO oxide films during melting and casting. MgO film on the surface could not act as a protective layer to prevent further oxidation and burning. Figure 1(d) shows the surface of 0.27% CaO added AM50 Mg composite during casting under an ambient atmosphere without SF₆ protective gas. No burning oxides and shiny surface appeared in 0.27% CaO added AM50 Mg composite, although it was cast without SF₆ protective gas, as shown in Figs.1(e) and (f). With below 0.3% CaO addition into commonly used AM50 Mg alloy, SF₆-free and even protective gas-free melting and casting processes can be possible.

3.2 Microstructures of CaO added AM50 Mg composites

Figure 2(a) shows the microstructure of as-cast AM50 Mg alloy. The microstructure of as-cast AM50 Mg alloy under non-equilibrium solidification consisted of the coarse primary α -phase dendrites and bulk skeletal β -phase divorced eutectic compounds, which mainly distribute at grain boundaries. Figure 2(b) shows the microstructure of 0.27% CaO added AM50 Mg composite. The microstructure and total volume fraction of the β -phase of 0.27% CaO added AM50 Mg composite were similar to those of AM50 Mg alloy because of

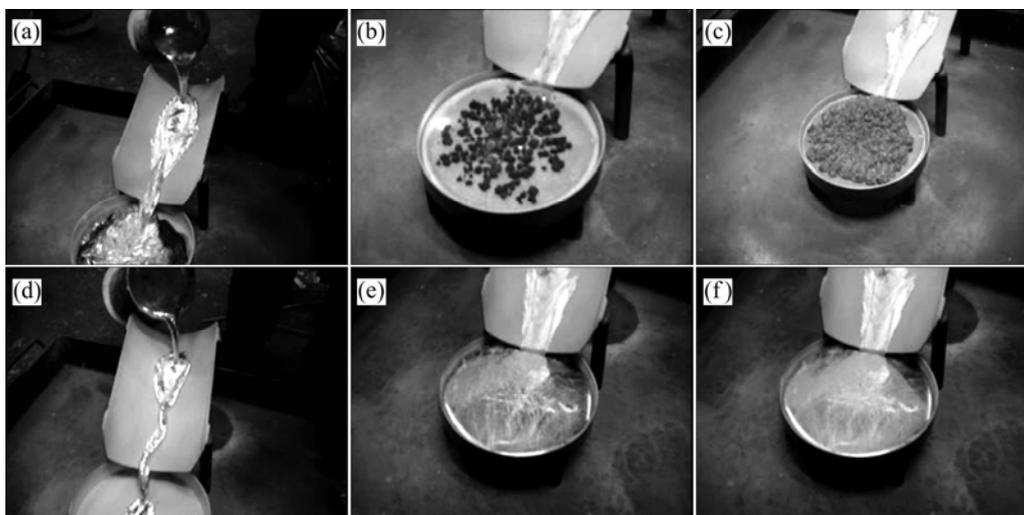


Fig.1 Surfaces of AM50 Mg alloys(a, b, c) and 0.27% CaO added AM50 Mg composites(d, e, f) during casting and solidification: (a), (d) 0 s; (b), (e) 40 s; (c), (f) 90 s

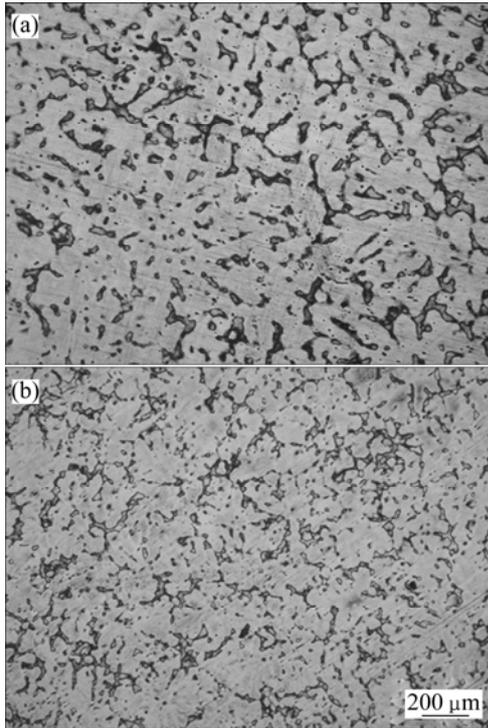


Fig.2 As-cast microstructures of AM50 Mg alloy(a) and 0.27%CaO added AM50 Mg composite(b)

0.27%CaO addition. Grain boundary consists of β -phase and Al_2Ca intermetallic compound. LEE et al[13–16] and KIM[17] used EPMA and TEM analyses to study the CaO behavior in AZ31 and AZ91D Mg alloys. It has been confirmed that CaO in Mg-Al alloys was reduced to Ca and then Al_2Ca phase formed without solid solution formation in Mg matrix even below solubility limit. CaO existed after reduction as Al_2Ca in Mg-Al alloys through EPMA and TEM analyses. However, the reason for the reduction of CaO and the formation of Al_2Ca in Mg-Al alloys could not be explained by thermodynamic mechanism.

3.3 Oxidation and burning resistance of CaO added AM50 Mg composites

Figure 3 shows the mass gain behaviors of AM50 Mg alloy and 0.27% CaO added AM50 Mg composite as a function of oxidation time at 500 °C in 7 h. As seen in Fig.3, the poor oxidation resistance of AM50 Mg alloy was exhibited. The results indicate that AM50 Mg alloy shows a parabolic law due to the loose and porous structure of MgO. On the contrary, the oxidation resistance of 0.27% CaO added AM50 Mg composite shows the stable oxidation behavior under the same conditions. Figure 4 shows the AES depth profile sputtered from the surface of AM50 Mg alloy and 0.27% CaO added AM50 Mg composite after oxidation

at 500 °C in 7 h. Figure 4(a) shows the AES depth profile of AM50 Mg alloy. In AM50 Mg alloy, it was confirmed that there was a thick MgO oxide layer on the surface. Figure 4(b) shows the depth profile of 0.27% CaO added AM50 Mg composite. In CaO added AM50 Mg composite, the surface scale consisted of the thin oxide layer mixed with MgO and CaO.

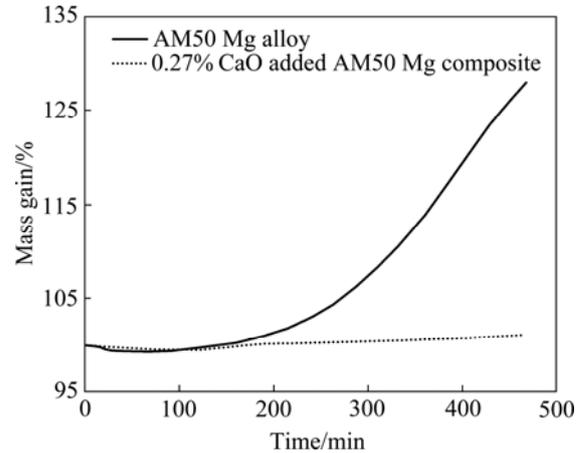


Fig.3 Mass gain curves of AM50 Mg alloy and 0.27% CaO added AM50 Mg composite

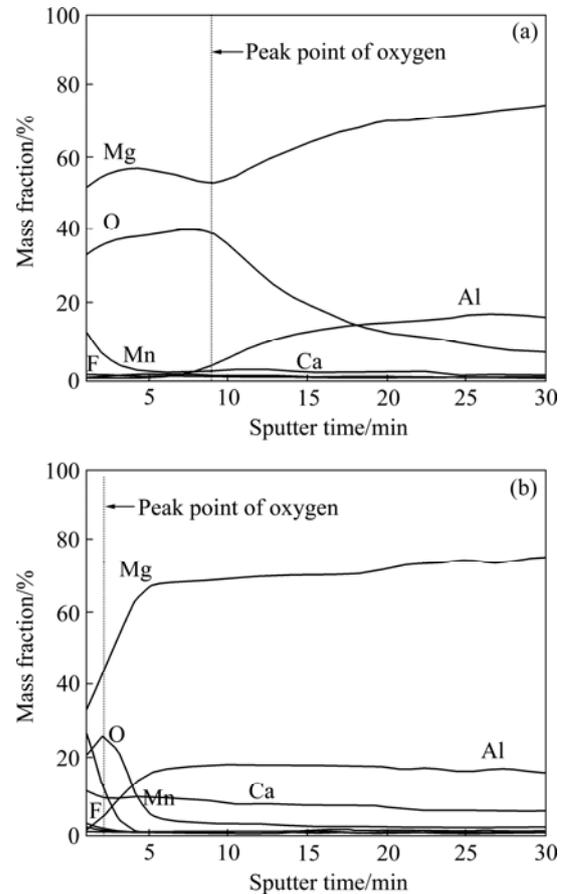


Fig.4 AES depth profiles sputtered from surface of AM50 Mg alloy and 0.27% CaO added AM50 Mg composite oxidized during TGA at 500 °C in 7 h

Figure 5(a) shows the result of the burning temperature under an ambient atmosphere at 700 °C. The burning temperature of 0.14% CaO added AM50 Mg composite was much higher than that of AM50 Mg alloy. With increasing CaO content, the burning temperature of CaO added AM50 Mg composite increased. Burning of Mg occurred because of porous MgO surface oxide film at high temperature. Oxidation behavior of Mg could be explained through Pilling-Bedworth ratio, R [19]. Pilling-Bedworth ratio means the ratio of oxide volume

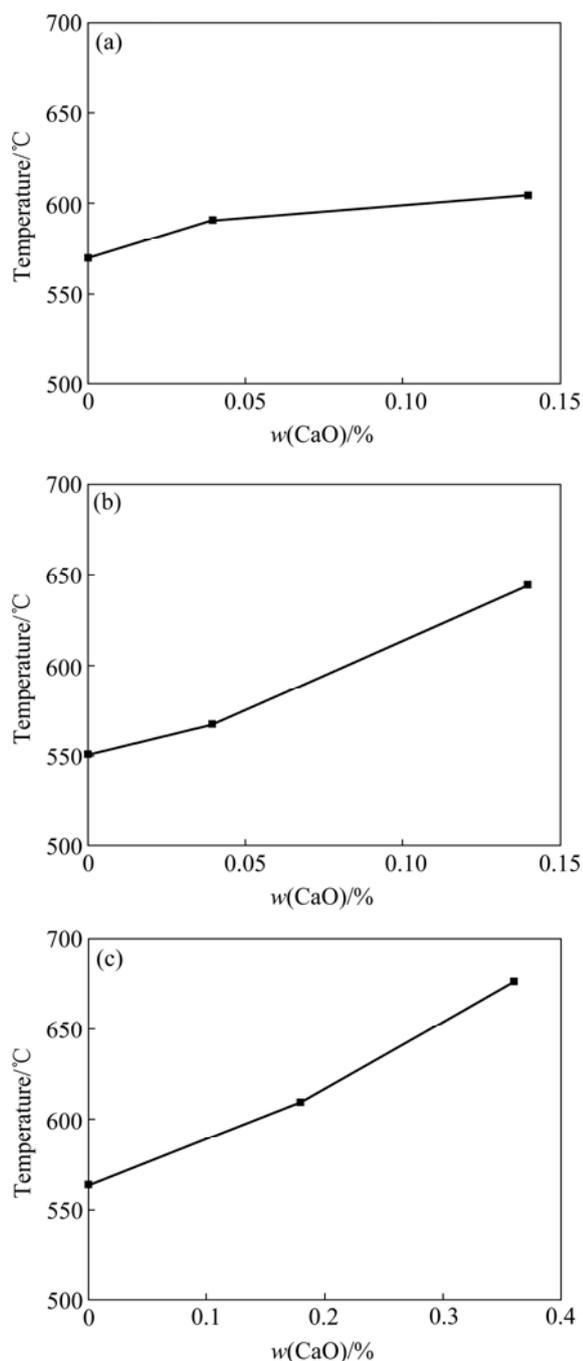


Fig.5 Burning temperatures for CaO added AM50 Mg composites under ambient atmosphere(a), nitrogen atmosphere(b) and dry air atmosphere(c)

to metal volume. Because the Pilling-Bedworth ratio for Mg is 0.83, MgO oxide film on the surface can not act as a protective layer to prevent oxidation and burning. Although CaO added Mg composite can not be explained by Pilling-Bedworth theory, the oxidation and burning resistance of CaO added AM50 Mg composite were increased due to the films which consist of polycrystalline CaO (0.78) and MgO (0.83)[20]. Figure 5(b) shows the results of the burning temperature under nitrogen atmosphere. Figure 5(b) shows the similar tendency with the results under an ambient atmosphere. Figure 5(c) shows the results of the burning temperatures for AM50 Mg alloy and 0.36% CaO added AM50 Mg composite under dry air atmosphere. The burning temperatures of AM50 Mg alloy and 0.36% CaO added Mg composite are 563 °C and 676 °C, respectively. The burning temperature of 0.36% CaO added AM50 Mg composite is much higher than that of AM50 Mg alloy and even over the melting temperature of AM50 Mg alloy.

4 Conclusions

1) Without SF_6 protective gas, the CaO added AM50 Mg composites could be well manufactured by conventional melting and casting procedures under an ambient atmosphere with shiny surface. CaO added AM50 Mg composites show the stable oxidation resistance by TGA procedure. From AES result, there is a thin oxide layer mixed with MgO and CaO in CaO added AM50 Mg composite.

2) With increasing CaO addition, the burning temperatures of CaO added AM50 Mg composites increase under ambient, nitrogen and dry air atmospheres. The oxidation and burning resistances of CaO added AM50 Mg composites are increased due to the films which consist of polycrystalline CaO and MgO.

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