OXIDATION BEHAVIOR OF Al₂Ca ADDED Al-5Mg ALLOY IN THE LIQUID STATE

Young-Ok Yoon, Seong-Ho Ha, Gil-Yong Yeom, Hyun Kyu Lim, Shae K. Kim
KITECH(Korea Institute of Industrial Technology); 156, Gaetbeol-ro, Yeonsu-gu; Incheon, 406-840, Korea South

Keywords: Al-5Mg, Al₂Ca, Oxidation, Liquid state

Abstract

The aim of the present study was to investigate the effect of Al₂Ca added Mg addition on the oxidation behavior of Al-5Mg alloy in the liquid state with TGA and melt oxidation test. Results of TG analysis showed that while the weight gain of Al-5Mg was 10%, Al₂Ca added Al-5Mg had the weight gain to 0.01%. Comparison between the surface and cross sectional appearance showed that there were a large number of pores and oxide clusters in Al-5Mg alloy, while pore was not observed in Al₂Ca added Al-5Mg alloy. SEM and EDS studies revealed that the formation of pores in Al-5Mg alloy was mainly due to the transformation of MgO to $MgAl_2O_4$ as the holding time was extended. In the case of Al₂Ca added Al-5Mg alloys, the existence of $MgAl_2O_4$ was not observed. On the other hand, MgO/CaO mixed layer existed and would act as a protective layer.

Introduction

The application of Al-Mg alloys has been extended in aerospace and automotive industries because of their light weight (low density), outstanding corrosion resistance, weldability and mechanical properties [1-3].

However, this alloy system shows poor oxidation resistance at high temperature. When Al-Mg alloy exposes to an ambient atmosphere at temperature above 350 °C, a dense, protective oxide layer covering the initial alloy surface is degraded rapidly and less protective oxide film is formed, consisting MgO and $MgAl_2O_4$ [4-7]. Especially, as molten state, the Al-Mg alloy has a fatal problem in process. Adding a large amount of Mg causes the formation of dross during melting process. The existence of dross degrades not only fluidity of the melt but also the mechanical properties and machinability of the final product. Its formation also reduces the Mg content in the melt because it mainly consists of Mg-oxide[8, 9]. To prevent the formation of such an oxide scale, sulfur dioxide (SO_2) is used commercially. Except for that, Be addition is a considerable way to improve the oxidation resistance of molten Al-Mg alloys, but limited due to its toxicity [9-13].

In an earlier study, it was reported that the oxidation resistance of the molten Al-Mg alloy was improved by the addition of Mg in the form of the master alloy including Al₂Ca [14, 15].

This paper is focused on an approach to effect of Al₂Ca existence on melting process. In the present study, oxidation behavior of Al₂Ca added Al-5Mg alloy was investigated and compared with that of Al₂Ca-free.

Experimental procedure

In this study, two Mg additives were examined: one is a pure Mg and another one is a Mg alloy including Al₂Ca. The alloys were melted by an electric resistance furnace at 750 °C and poured into the mold in the size of Ø52×270mm. The sample for melt oxidation test was machined in the form of a billet with the size of Ø24×30mm. The machined samples were cleaned with ethyl alcohol and pickled with 5% Nital. And then, the samples were put into alumina crucible and melted in electric resistance furnace at 720 °C under an ambient atmosphere. After holding for 0~6hr, they were air-cooled. TGA (thermogravimetric analysis) was carried out to measure weight gain with holding time. The surface of the samples after the melt oxidation test was analyzed with SEM-EDS.

Table I shows the chemical compositions of as-cast ingots by ICP analysis. As can be seen in Table I, Al₂Ca added Al-5Mg alloy has about 0.03wt.%Ca. The experimental conditions for the TGA analysis and melt oxidation test are given in Table II.

Table I. Chemical compositions of the alloys

	Al	Mg	Ca
Al-5Mg	94.96	4.91	-
Al₂Ca added Al-5Mg	94.93	4.88	0.03

Table II. Experimental conditions for oxidation test

	Thermogravimetric analysis	Electric resistance furnace
Holding temp.	720 °C	
Holding time	0 ~ 6 hr	
Atmosphere	Dry air	Air
Crucible	Alumina	
Specimen size	2x2x1 [mm]	Ø24x30mm

Results and Discussion

Figure 1 shows the melt surface of two examined alloys during the melting process in the electric resistance furnace: (a) surface after adding pure Mg into molten pure Al and (b) surface after adding Al₂Ca added Mg into molten pure Al, respectively. From the Figure 1(a), it was confirmed that the oxide clusters were formed after the ignition and oxidation with the Mg addition. On the other hand, in the case of Al₂Ca added Al-5Mg alloy, clean melt surface was shown, indicating that the thin dense oxide layer was formed on the surface. From this, it is considered that the melt protection effect shown in Al₂Ca added Al-5Mg alloy can not only lead to improvement of melt soundness and mechanical properties of the final product but also, have a good effect on the alloy recycling.

For Al-Mg alloy with large amount of Mg content, generally, protective gas such as SO_2 and Be addition are considered to

protect melt [4-7]. However, the melting process without the use of protective gas and Be addition would be possible through the Al₂Ca addition.

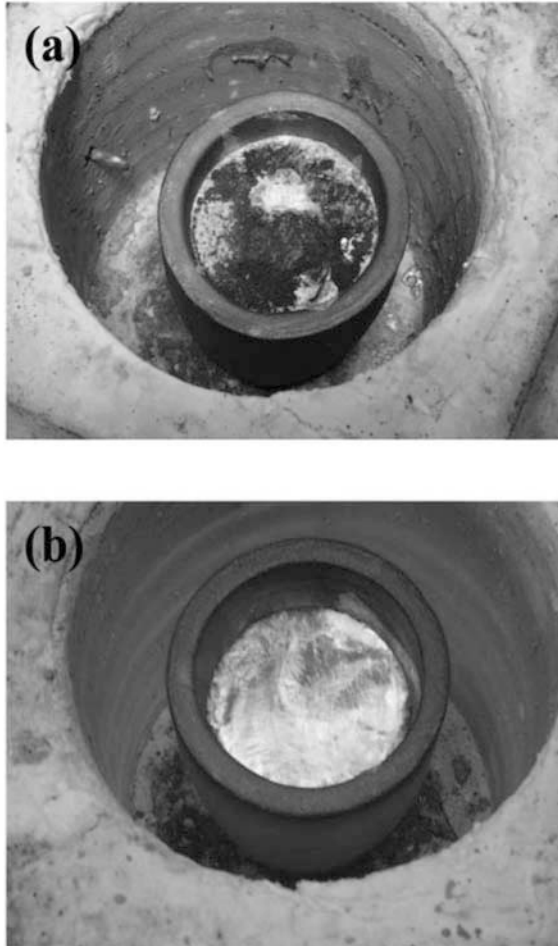Figure 1. Melt surface of (a) Al-5Mg and (b) Al₂Ca added Al-5Mg alloys.
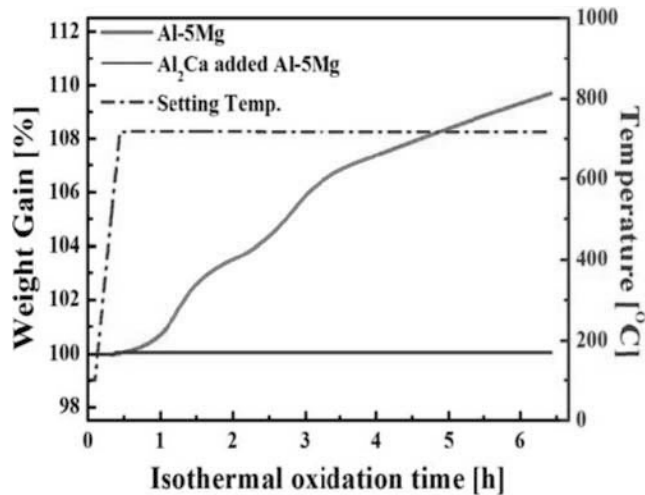

Figure 2. TGA results of Al-5Mg and Al₂Ca added Al-5Mg alloys.

Figure 2 shows the TGA result of two examined alloys at 720°C under a dry air ambient atmosphere for 6hr. Al-5Mg alloy showed the rapid weight gain, following the parabolic rate law. On the other hand, in the case of Al₂Ca added Al-5Mg alloy, there was no visible weight change, indicating the oxidation resistance was improved.

The photograph for the riser and cross section of the specimens after melt oxidation test are shown in Figure 3 and 4. For the riser part, the alloys showed no significant change as the holding time was extended.

However, in the cross section, Al-5Mg alloy had oxide inclusions at 3 and 6hr, while the Al₂Ca added Al-5Mg alloy showed no defect through all the holding time. The formation of these inclusions in the Al-5Mg alloy would be attributed to the adulteration with oxide clusters formed during the Mg addition.
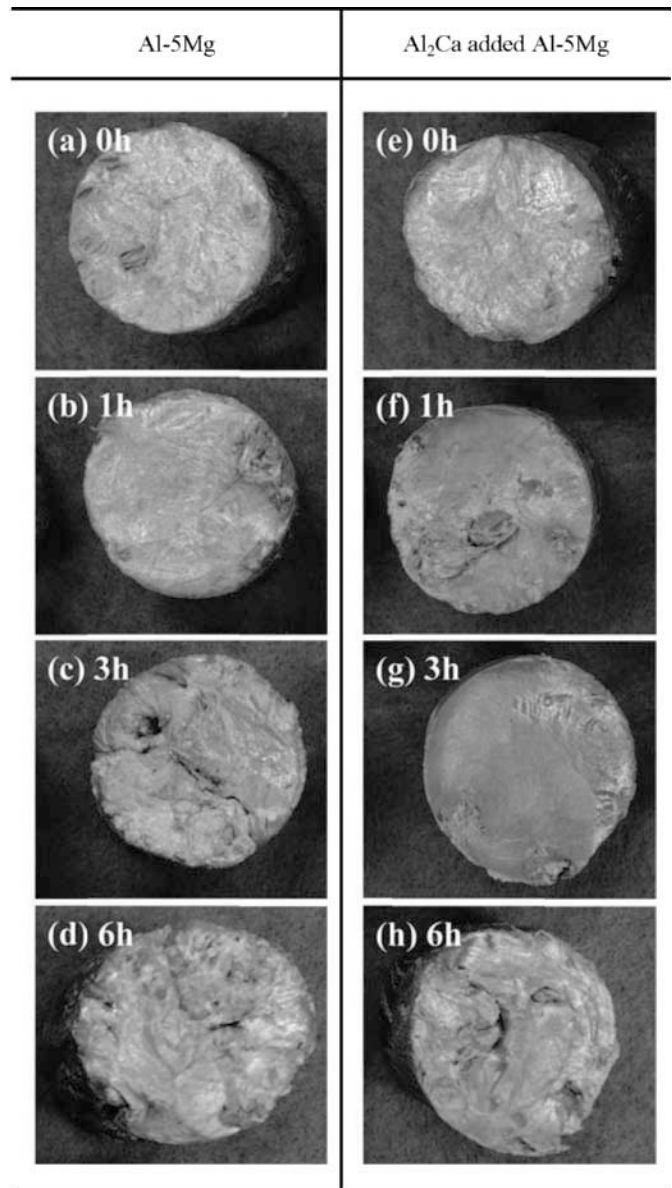
Figure 3. Risers of (a-d) as-cast Al-5Mg
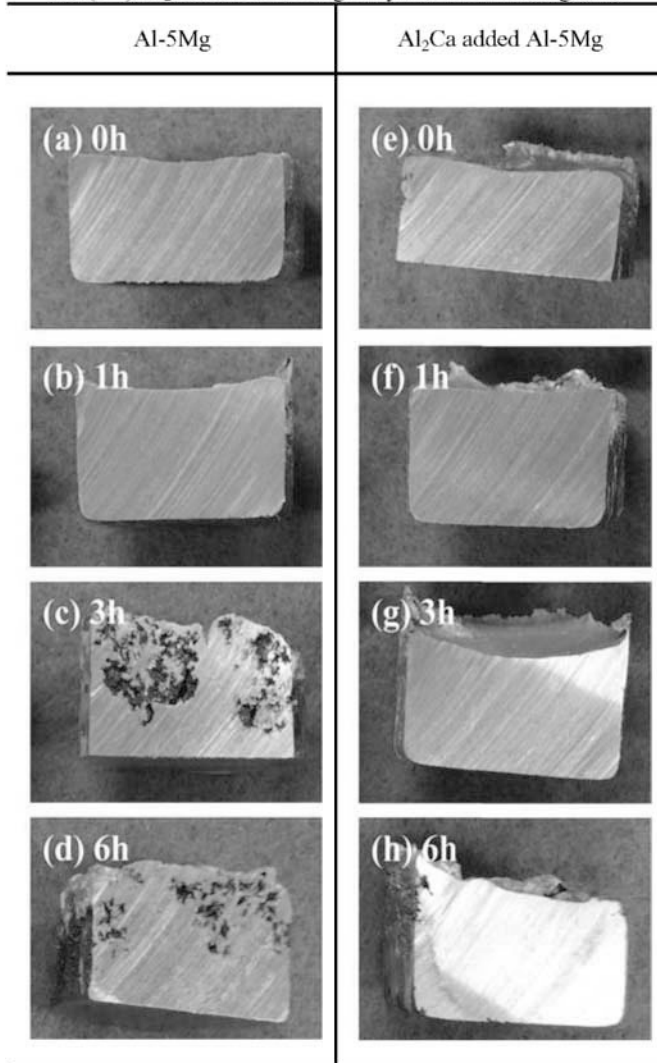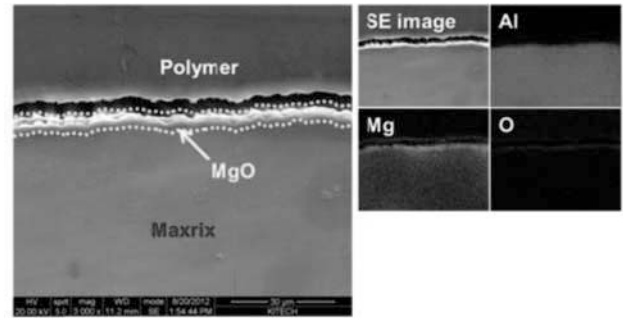and (e-h) Al₂Ca added Al-5Mg alloys for each holding time.

Figure 4. Cross sections of (a-d) as-cast Al-5Mg
and (e-h) Al₂Ca added Al-5Mg alloys for each holding time.

Figure 5 shows the results of the mapping by SEM-EDS for Al-5Mg alloy. As shown in Figure 5(a), it can be confirmed that an oxide layer regarded as MgO is formed on the surface at 0hr. After the holding for 6hr, Mg-Al based oxide scale are shown and considered as MgAl₂O₄, observed generally on the surface of Al-Mg based alloys [5, 8, 9].

Al₂O₃ and MgO oxide layers are formed on the surface of Al-Mg based alloy during melting and form spinel MgAl₂O₄ phase with changing variables such as time and temperature [17].

Figure 6 shows the results of the mapping by SEM-EDS for Al₂Ca added Al-5Mg alloy. In the case of 0hr, there exists the MgO layer on the surface, similar to that of Al-5Mg alloy, shown in Figure 6(a). After the holding for 6hr, differently with that of Al-5Mg alloy, the existence of MgAl₂O₄ was not observed.

On the other hand, the oxide layer on the surface appeared to consist of MgO and CaO (see Figure 6(b)). Such an improvement of the oxidation resistance in Al₂Ca added Al-5Mg alloy would be attributed to the formation of dense MgO/CaO mixed layer [2, 23-24].
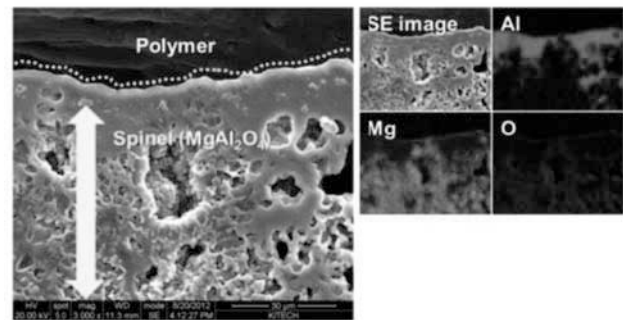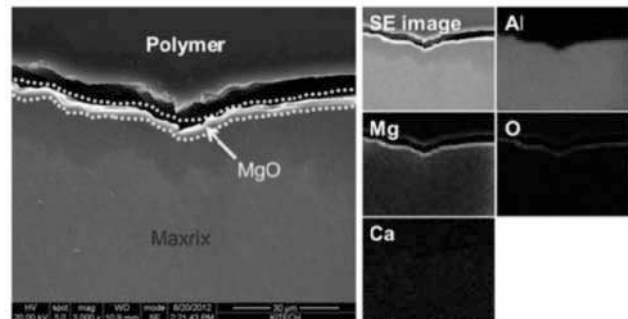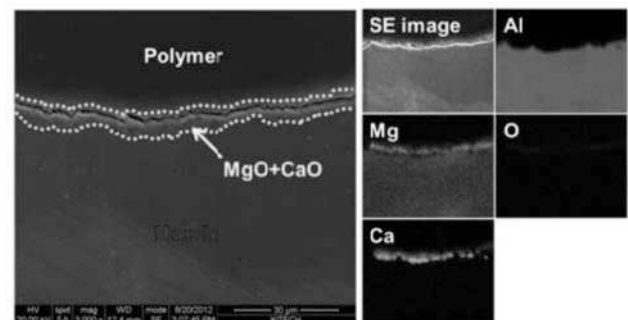

Figure 5. SEM-EDS mapping results of Al-5Mg alloy for each holding time.

Figure 6. SEM-EDS mapping results of Al₂Ca added Al-5Mg alloy for each holding time.

Conclusion

In the present study, the oxidation behavior of Al-5Mg and Al_2Ca added Al-5Mg alloys was evaluated in molten state.

Results of TG analysis showed that while the weight gain of Al-5Mg was 10%, Al_2Ca added Al-Mg had the weight gain to 0.01%. Comparison between the riser and cross sectional appearance showed that there were a large number of pores and oxide clusters in Al-5Mg alloy, while pore was not observed in Al_2Ca added Al-5Mg alloy.

SEM and EDS studies revealed that the formation of pores in Al-5Mg alloy was mainly due to the transformation of MgO to $MgAl_2O_4$ as the holding time was extended. In the case of Al_2Ca added Al-5Mg alloys, the existence of $MgAl_2O_4$ was not observed. On the other hand, MgO/CaO mixed layer existed and would act as a protective layer.

Reference

1. Y. Oishi et al., "Development of High Strength Magnesium Alloy Wire," *Sei Technical Review*, 2003, no. 56:54-58
2. O.A. Kaibyshev, *Superplasticity of Commercial Aluminium Alloys* (Moscow, Metallurgiya, 1984), 37–51.
3. O. Ozdemir, J.E. Gruzleski, and R.A.L. Drew, "Effect of Low-Levels of Strontium on the Oxidation Behavior of Selected Molten Aluminum–Magnesium Alloys", *Oxid Met*, 72 (2009), 241–257.
4. D.J. Field, G.M. Scamans, and E.P. Butler, "The High Temperature Oxidation of Al-4.2 Wt Pct Mg alloy", *Metallurgical Transactions A*, 18A (3) (1987) 463-472.
5. M.H. Zayan, O.M. Jamjoom, and N.A. Razik, "High-Temperature Oxidation of Al-Mg Alloys", *Oxidation of Metals*, 34 (3-4) (1990), 323-333.
6. K. Shimizu et al., "The Early Stages of High Temperature Oxidation of an Al-0.5wt% Mg Alloy", *Corrosion Science*, 40 (4/5) (1998), 557-575.
7. F.H. Samuel et al., "Influence of Composition, Sr Modification, and Annealing Treatment on the Structure and Properties of Cast Al-4 pct Mg Alloys", *Metallurgical and Material Transcation*, 34A (1) (2003), 115-129.
8. I. Haginoya, and T. Fukusako, "Oxidation of Molten Al-Mg Alloys", *Transactions of the. Japan Institute of Metals*, 24 (9) (1983), 613-619.
9. D.L. Belitskus, "Oxidation of Molten Al-Mg Alloy in Air, Air-SO_2, and Air-H_2S Atmospheres", *Oxidation of Metals*, 3 (4) (1971), 313-317.
10. C. Houska, "Beryllium in Aluminum and Magnesium Alloys", *Metals and Materials*, 4 (2) (1988), 100-104.
11. L.F. Mondolfo, *Aluminum Alloys: Structure & Properties* (London, Butterworth & Co. Ltd., 1976),
12. Y. Wang, and Y. Xiong, "Effects of Beryllium in Al–Si–Mg–Ti Cast Alloy", *Materials Science and Engineering : A*, 280 (1) (2000), 124–127.
13. David H. DeYoung, and J. Peace, "Beryllium in Dross Produced during Aluminum Melting", *Light Metals 2009*, (2009), 659-664.
14. J.K. LEE, and S.K. KIM, "Effect of CaO Composition on Oxidation and Burning Behaviors of AM50 Mg Alloy", *Transactions of Nonferrous Metals Society of China*, 21 (2011), s23–s27.
15. J.K. Lee, Y.O. Yoon, S.K. Kim, "Development of CaO Added Wrought Mg Alloy for Cleaner Production", *Magnesium Technology 2006*, (2006), 185-189.
16. S.K. Kim, J.K. Lee, Y.O. Yoon, H.H. Jo, "Development of AZ31 Mg alloy wrought process route without protective gas", *Journal of Materials Processing Technology*, 187-188 (2007), 757-760.
17. C.N. Cochran, D.L. Belitskus, and D.L. Kinosz, "Oxidation of Aluminum-Magnesium Melts in Air, Oxygen, Flue Gas, and Carbon Dioxide", *Metallurgical Transcation B*, 8B (1) (1977), 323-332.