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INFLUENCE OF Si ADDITION ON OXIDE GROWTH OF Al-6 MASS%Mg ALLOY MELTS

Influence of Si addition on oxide layer growth of Al-6 mass%Mg alloys in molten state was investigated in this study. After melt holding for 24 h, the melt surface of only Si-free alloy became significantly bumpy, while no considerably oxidized surface was observed even with 1 mass%Si addition. There was no visible change on the appearance of melt surfaces with increasing Si content. As a result of compositional analysis on the melt samples between before and after melt holding, the Si-added alloys nearly maintained their Mg contents even after the melt holding for 24 h. On the other hand, the Mg content in the Si-free alloy showed a great reduction. The bumpy surface on Si-free alloy melt showed a large amount of pores and oxide clusters in its cross-section, while the Si-added alloy had no significantly grown oxide clusters on the surfaces. As a result of compositional analysis on the surfaces, the oxide clusters in Si-free alloy contained a great amount of Mg and oxygen. The oxide layer on the Si-added alloy was divided into Mg-rich and Mg-poor areas and contained certain amounts of Si. Such a mixed oxide layer containing Si would act as a protective layer during the melt holding for a long duration.

Keywords: Al-Mg system, Si addition, Oxidation, Phase diagram

1. Introduction

Al-Mg alloys are widely used in the automotive and ship building industries because of their excellent corrosion resistance and good mechanical properties [1]. The main strengthening mechanisms of Al-Mg alloys can be explained by solid solution strengthening and work hardening [1]. Their strengthening effect is maximized by deformation processes, while the strength of castings is limited because they are non-heat treatable. Therefore, alloy design using the addition of third elements is considered to further improve the strength of Al-Mg alloy castings by precipitation hardening. Si is a main alloying element used in majority of commercial Al alloys and its addition into Al-Mg alloys possibly provides an effective strengthening by Mg₂Si precipitations, the improvement of castability, and further weight reduction [1].

Al-Mg alloys in liquid state are rapidly oxidized during melting and casting processes when they are exposed to oxidizing atmosphere [2-5]. The addition of Mg in Al alloy forms an MgO oxide layer, which is further followed by the formation of MgAl₂O₄ spinel. A high content of Mg results in an increase of oxide growth rates and entrainment of a large quantity of oxide inclusion into the melts [2-5]. Al-Mg alloys are initially oxidized with a low oxidation rate, while, after a period of time (depending

on Mg content and temperature), a sudden increase in the oxidation rate takes place, which is known as breakaway oxidation [2-5]. Addition of a trace amount of Be have been considered to reduce both the Mg oxidation and delay the beginning of breakaway oxidation [6]. This leads to a reduction of the amount of Mg loss and oxide inclusions that are possibly entrained into the melt during casting [6]. It has been also reported that the addition of Ca by using Mg+Al₂Ca master alloy can significantly improve the oxidation resistance of Al-Mg alloys [4,7-8].

As aforementioned, the Si addition has been considered not only for the improvement of mechanical properties and castability in Al alloys [1], but also for the increase of oxidation resistance in various metallic materials [9-11]. According to a previous report [12], it was shown that the Si addition into Al-Mg alloys increased the oxidation resistance in solid state. The Mg₂Si phase in the Al-Mg-Si alloys examined was formed during solidification was believed to be associated with the improvement of oxidation resistance [12]. However, the oxidation resistance of the alloys is still questionable in molten states, which all constituent elements are soluble and no intermetallic phase is present. In this study, influence of Si addition on oxide layer growth of Al-Mg alloy containing high contents of Mg in a molten state was investigated.

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2. Experimental

In this study, the composition of base metal is Al-6 mass%Mg, in which the Mg content is similar to the lower limit in the specifications of 535.0 Al casting alloy [1]. Alloys were made in an induction furnace under ambient atmosphere. Pure Al was melted in a graphite crucible at 750°C and 6 mass% of pure Mg was added into the melt. Then, 1, 3, 5, and 7 mass%Si in the form of Al-25mass%Si master alloy were added into each charge, respectively. After that, the melts were held at 750°C for 24 h. The surface changes before and after melt holding for 24 h were observed depending on the Si content. After the melt holding for 24 h, the alloy melts were brought out from the furnaces and air-cooled. The alloy ingots air-cooled were cross-sectioned to examine the surface oxide layers. The amount of Mg loss by

formation of Mg-based oxides in the base metal was examined by inductively coupled plasma optical emission spectroscopy (ICP-OES). Oxide areas entrained inside in cross-sections of the samples were observed and analyzed using field emission (FE) - scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) detector. Phase equilibria between the alloys and O₂ at 700°C were calculated by *FactSage 7.3* to examine the oxide formation depending on Si content [13].

3. Results and discussion

Melt surfaces of examined alloys after holding for 24 h are shown in Fig. 1. After 24 h, the melt surface of Si-free alloy

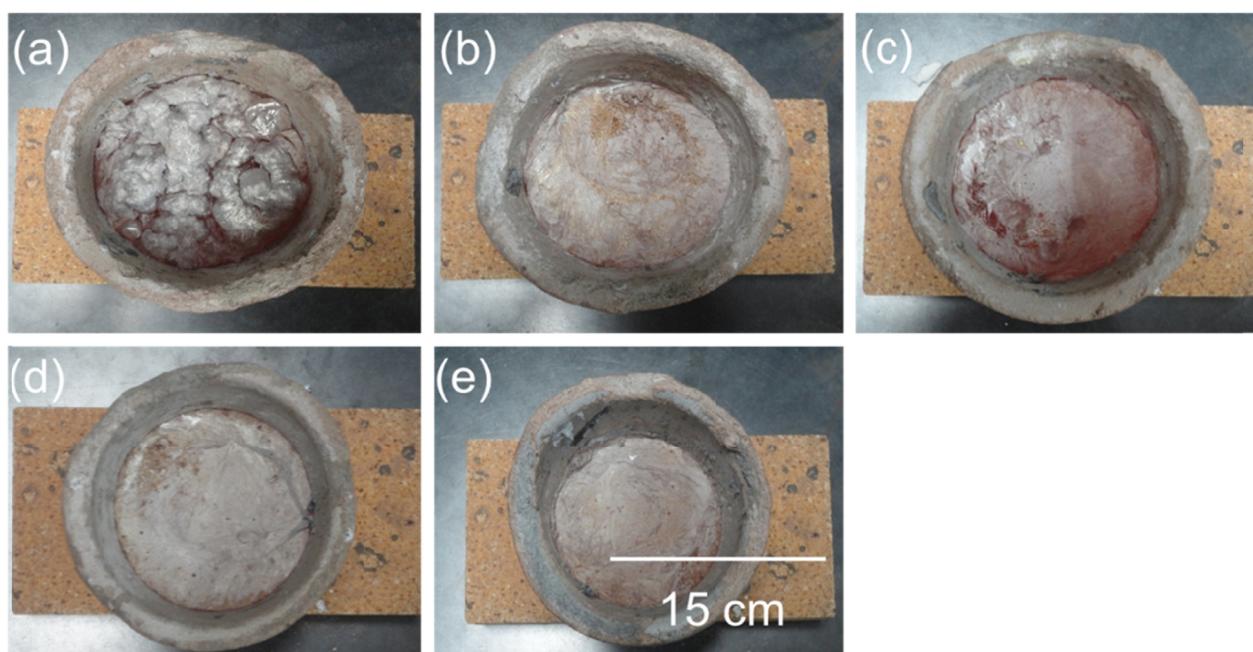


Fig. 1. Melt surfaces of examined alloys after holding for 24 h. (a) Al-6 mass%Mg, (b) Al-6 mass%Mg-1 mass%Si, (c) Al-6 mass%Mg-3 mass%Si, (d) Al-6 mass%Mg-5 mass%Si, and (e) Al-6 mass%Mg-7 mass%Si alloys

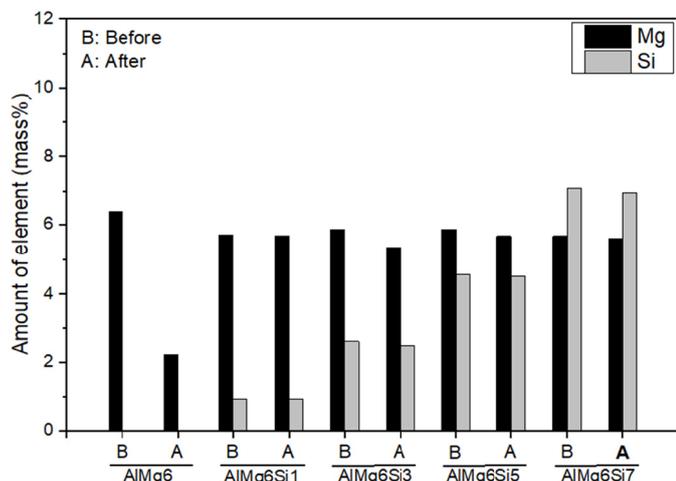


Fig. 2. Compositional variations between before and after melt holding for 24 h of examined alloys

became significantly bumpy, indicating that it included a large amount of pores inside near the surface. However, even with 1 mass%Si addition, no considerably oxidized surface was observed. And also, there was no visible change on the appearance of melt surfaces with increasing the Si content.

Fig. 2 shows compositional variations between before and after melt holding for 24 h of cross-sections of examined alloys. The Si-added alloys nearly maintained their Mg content even after the melt holding for a long duration. This might be attributed to the surface protection effects shown in Fig. 1. On the other hand, the Mg content in the Si-free alloy showed a great reduction after 24 h, implying the reduced Mg would be consumed to form large amounts of Mg-based oxides.

Fig. 3 displays SEM-backscattered electron (BSE) images of the cross-sections oxidized at 500°C. The oxidized cross-section of Si-free alloy melt after 24 h showed coarse and dark

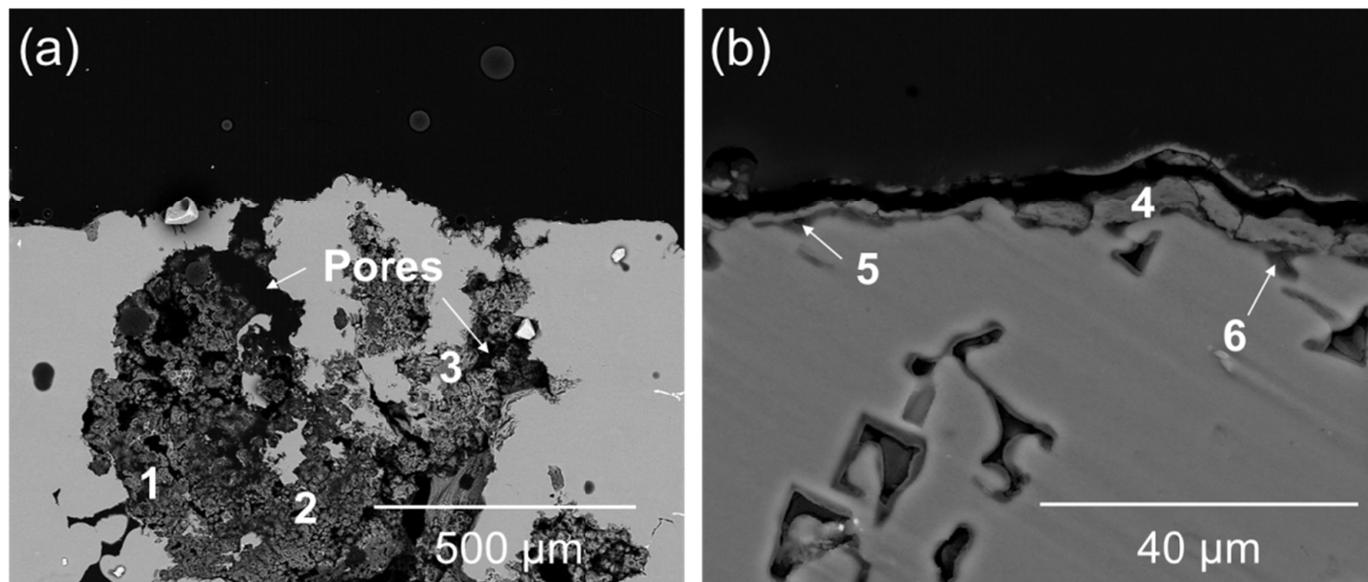


Fig. 3. SEM-backscattered electron (BSE) image of cross-sections oxidized during melt holding at 700°C for 24 h. (a) Al-6 mass%Mg and (b) Al-6 mass%Mg-7 mass%Si alloys

areas including a large amount of pores significantly grown from the surface to inside. The bumpy surface on Si-free alloy melt shown in Fig. 1 would be attributed to the agglomeration of pores near the surfaces. Since the elements with higher atomic numbers backscatter electrons more strongly than those with lower atomic numbers, the dark areas except for the pores were considered as Mg-based oxides. On the other hand, the Si-added alloy had no significantly grown oxide clusters on the surfaces.

Compositional analysis of the numbered areas shown in Fig. 3 by SEM-EDS is given in Table 1. Areas numbered as 1 and 2 contained a great amount of Mg and oxygen, while the relatively bright part numbered as 3 in the oxide area included 14.50 mass%Al. The formation of such highly Mg-enriched oxides would lead to a significant reduction of Mg in the base metal shown in Fig. 2. However, the oxide layer on the Si-added alloy can be divided into Mg-rich (numbered as 4) and Mg-poor (numbered as 5 and 6) areas based on the compositional information shown in Table 1.

TABLE 1

Compositional analysis of areas shown in Fig. 3 by SEM-EDS

Area	Analyzed composition (mass%)			
	Al	Mg	Si	O
1	—	80.19	—	19.81
2	—	72.54	—	27.46
3	14.50	60.70	—	24.80
4	10.59	62.42	2.18	24.80
5	41.36	23.04	24.05	11.55
6	46.51	19.50	20.75	13.24

The Mg-rich and Mg-poor areas corresponded to the upper and lower layers, respectively. The upper layer contained a trace

amount of Si, whereas much higher content of Si was included in the lower layer. The mixed oxide layer containing Si would act as a protective layer during the melt holding for a long duration.

Phase equilibria between three different base metals and O₂ at 700°C calculated by *FactSage 7.3* are shown in Fig. 4. These calculations indicated that the MgO was the first formed oxide in all cases as O₂ fraction increased. However, Al-6 mass%Mg-7 mass%Si alloy formed only negligible amount of MgO. After a consumption of Mg to form MgO, great amounts of spinel were formed in all examined alloys following the further increase of O₂ fraction. During long time exposures, the growths of oxides on the surfaces are attributed to the oxygen diffusion into the matrix through the external oxide layers. The continuous diffusion of oxygen can also lead to the accumulation of oxygen and formation of pores as shown in Fig. 3(a). The MgO and spinel are considered non-protective in long-term oxidations [2-5] and possibly provide the diffusion pathways of oxygen. On the other hand, the formation of multi-element oxide containing Si occurred in Si-added alloys and was only difference between Si-free and Si-added alloys. Therefore, the oxide layer on the Si-added alloy aforementioned would be comprised of MgO, spinel, and Si-containing oxides. As mentioned above, Al-Mg alloys exhibit low oxidation rates in initial oxidation [7]. The oxide layer in this stage can affect the oxidation resistance in further oxidations. It was considered that the oxide layer mixed with the Si-based oxides mentioned above can degrade the pathways for oxygen diffusion into matrix. As shown in the SEM-EDS results, the Mg-rich and Mg-poor areas were found on the surface of Si-added alloy. The Mg-rich outmost layer was regarded as the primary oxide layer, which is formed identically in the Si-free alloy, while the Mg-poor lower layer containing a great amount of Si would prevent the further growth of Mg-rich outmost layer.

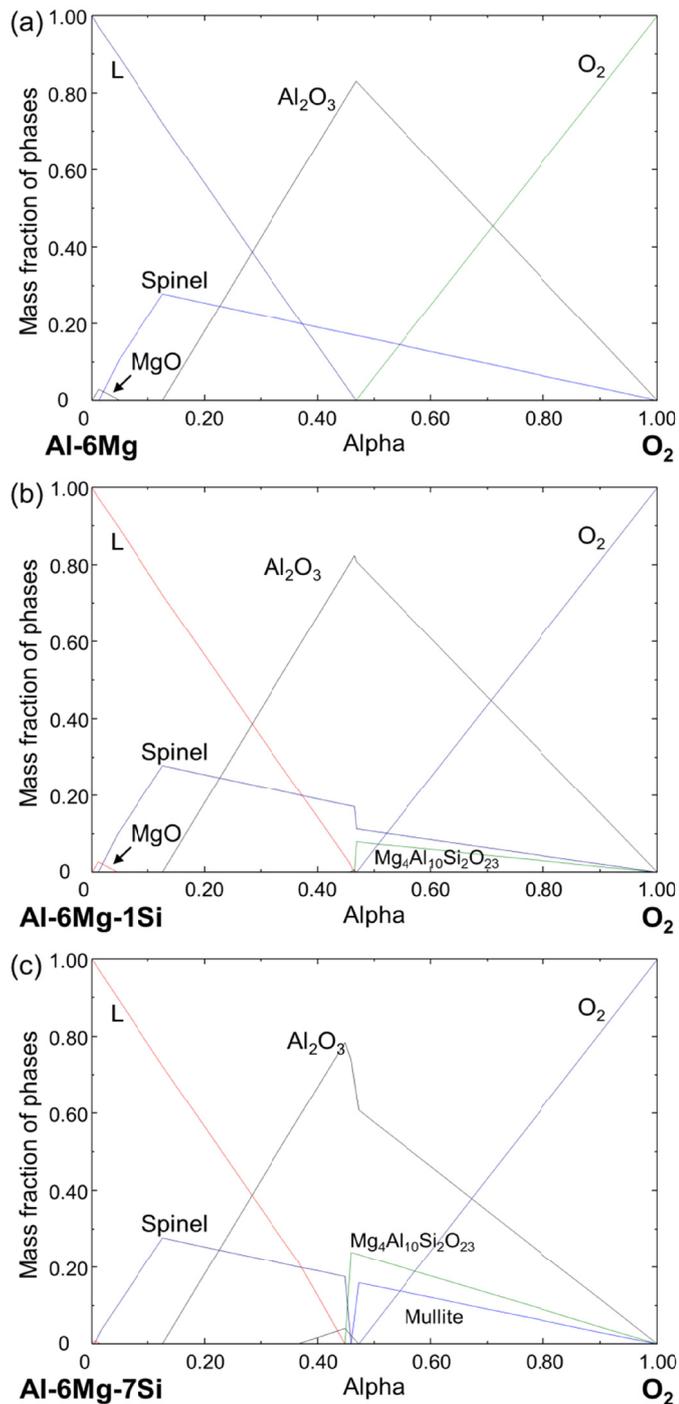


Fig. 4. Phase equilibria between (a) Al-6 mass%Mg and O_2 , (b) Al-6 mass%Mg-1 mass%Si and O_2 , and (c) Al-6 mass%Mg-7 mass%Si and O_2 at 700°C calculated by *FactSage 7.3*

4. Conclusions

After melt holding for 24 h, the significantly bumpy surface was observed in only Si-free alloy, while there was no considerably oxidized surface even with 1 mass%Si addition. No visible change on the appearance of melt surfaces was found with increasing Si content. As a result of compositional analysis

on the melt samples between before and after melt holding, the Si-added alloys nearly maintained their Mg contents throughout the melt holding for 24 h. On the other hand, the Si-free alloy showed a great reduction in the Mg content. The cross-section of Si-free alloy melt showed a large amount of pores and oxide clusters, while the Si-added alloy had no significantly grown oxide clusters on the surfaces. From the result of compositional analysis on the surfaces by SEM-EDS, it was found that the oxide clusters in Si-free alloy contained a great amount of Mg and oxygen. The oxide layer on the Si-added alloy was divided into Mg-rich and Mg-poor areas as upper and lower layers, respectively, and contained certain amounts of Si. Based on the phase diagrams calculated, the oxide layer on the Si-added alloy was comprised of MgO, spinel, and Si-containing oxides. The mixed oxide layer containing Si would act as a protective layer during the melt holding for a long duration.

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