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Featured Letter

Effect of Ca addition on selective oxidation of Al_3Mg_2 phase in Al-5 mass% Mg alloy

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This study examined the effect of Ca addition on the selective oxidation of the Al_3Mg_2 phase in an Al-5 mass%Mg alloy during oxidation at 400 °C and 500 °C for 72 h. Ca addition led to the formation of the Al_4Ca and Laves_C36 phases besides the primary Al solid solution and Al_3Mg_2. After the oxidation test, there was no significant oxidation in both the Ca-free and Ca-added alloy samples and no visible change in the surfaces between them at 400 °C, which is lower than the melting temperature of Al_3Mg_2 (451 °C). At 500 °C, the surface of the Ca-free alloy showed the formation of oxide blisters, which was not observed in the Ca-added alloy. The presence of an Al_4Ca phase at the grain boundaries led to the formation of multi-element oxides containing Al, Mg, and Ca, which can contribute to the formation of a compact oxide layer.

1. Introduction

Al-Mg alloys are widely used in marine, transport, and chemical engineering [1–3]. They are active when exposed to air or come into contact with oxygen [4–6]. The maximum content of Mg in commercial Al-Mg alloys is about 5 mass% in the AA5xxx series [1]. The as-cast microstructure of the Al-Mg alloy consists of predominant α-Al dendrites and a fully divorced β-Al_3Mg_2 phase in the interdendritic regions [7]. As the Mg content increases, the alloy density decreases, the strength increases, and the ductility decreases due to the formation of a brittle β-Al_3Mg_2 phase. Mg is selectively oxidized at elevated temperatures, and such selective oxidation, which is prominent at the grain boundaries due to the presence of Al_3Mg_2, causes the formation of oxide inclusions. Ca is one of the additives that can be used to reduce Mg oxidation [8–10]. Ca addition also forms Ca-based intermetallic compounds via eutectic reactions [11]. Studying the behavior of Ca-based phases in oxidation can provide an understanding of the surface passivation mechanism during the heat treatment and/or melting of Al-Mg alloys. In Al-Mg systems, the β-Al_3Mg_2 phase formed at grain boundaries by eutectic reactions can drastically influence surface oxidation at elevated temperatures due to tis low melting point (451 °C) and high Mg content. The aim of this study is to investigate the effect of Ca addition on the selective oxidation of Al_3Mg_2 in an Al-5 mass% Mg alloy, whose Mg content corresponds to that of the AA5356 alloy [1].

2. Experimental procedures

Alloy samples were made in an induction furnace under an ambient atmosphere. Pure Al was melted in a graphite crucible with an electric resistance furnace at 700 °C under ambient atmosphere. Pure Mg and the Mg + Al_2Ca master alloy [12] were added into the melt. Then, the alloys were cast into a steel mold that was preheated to 200 °C. Surface oxidation of the as-cast samples was performed at 400 °C and 500 °C for 72 h to investigate the effect of Ca below and above the melting temperature of Al_3Mg_2, which is 451 °C (1 °C higher than the eutectic temperature 450 °C) [13], for a long-time exposure. The oxide surface formed on the air-cooled samples was analyzed using scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDS). Phase diagrams for the oxygen partial pressure to predict the formation of the oxide layer and the Scheil cooling of the Al-Mg-(Ca) system were calculated using Factsage 7.1 [14].

3. Results and discussion

The calculated solidification path of the Al-5 mass% Mg-0.3 mass% Ca alloy is presented in Fig. 1. Solidification begins at 631.60 °C and ends at 448.43 °C. According to the calculated diagram, the solidification sequence is Liquid → FCC_Al at 631.60 °C,

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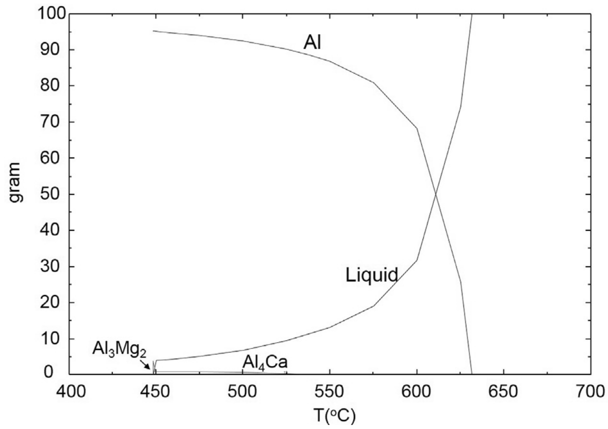

Fig. 1. Scheil cooling calculation of the Al-5 mass% Mg-0.3 mass% Ca alloy using FactSage 7.1.

Liquid → FCC_Al + Al_4Ca at 538.37 °C, Liquid → FCC_Al + Laves_C36 at 458.64 °C, and liquid → FCC_Al + Laves_C36 + Al_3Mg_2 invariant eutectic reaction at 448.43 °C. Thus, the as-cast microstructure of the Al-5 mass% Mg-0.3 mass% Ca alloy consists of α-Al, Al_4Ca, Al_3Mg_2 and a trace amount of Laves_C36.

SEM images of the sample surfaces oxidized at 400 °C and 500 °C are shown in Fig. 2. Each number presented in Fig. 2 also refers to the regions analyzed by EDS. At 400 °C, which is lower than the melting temperature of Al_3Mg_2 [13], no significant oxidation in both samples and no visible change in the surfaces between Al-5 mass% Mg and Al-5 mass% Mg-0.3 mass% Ca alloys are observed. According to the SEM-EDS results summarized in Table 1, there is no notable difference in the Mg concentration between the Al-5 mass% Mg and Al-5 mass% Mg-0.3 mass% alloys (regions 1 and 2, respectively) and no Ca is detected, even in the Ca-added alloy sample. Therefore, in α-Al matrix, a negligible amount of Ca dissolves and is involved in surface segregation and oxide layer formation.

The surface of the Al-5 mass% Mg alloy after oxidation at 500 °C shows the formation of oxide blisters, which might grow into cauliflower-like oxides [15]. This occurs mainly at the Al_3Mg_2 phase containing the highest Mg content in the microstructure. According to a previous study [15], the formation of the blisters can be explained as the creation of a high inward vacancy migration by high outward diffusion of Mg atoms during the rapid growth of the surface oxide layer. This finally forms voids at the metal-oxide interface. A continuous growth of the voids would eventually reduce oxide adhesion and blister formation. A further oxidation would break the blisters, giving rise to cauliflower-like oxides. Oxide blisters can also lead to the formation of surface cracks, further accelerating the oxidation. As shown by the EDS results for regions 3 and 4 in Table 1, the blisters have much higher contents of Mg and O, indicating that a MgO-rich oxide layer is formed. However, no blister is observed at the surface of the Ca-added alloys sample. It is worth nothing that Ca is segregated at the grain boundaries. Therefore, Ca is considered to suppress blister formation at the grain boundaries of the Ca-added alloy sample.

Fig. 3 shows the phase diagrams of temperature versus oxygen partial pressure in (a) Al_3Mg_2-O_2 and (b) Al_4Ca-O_2 calculated using Factsage 7.1. The oxide formation with lower oxygen partial pressure is preferential. Fig. 3(a) displays the formation of MgO and

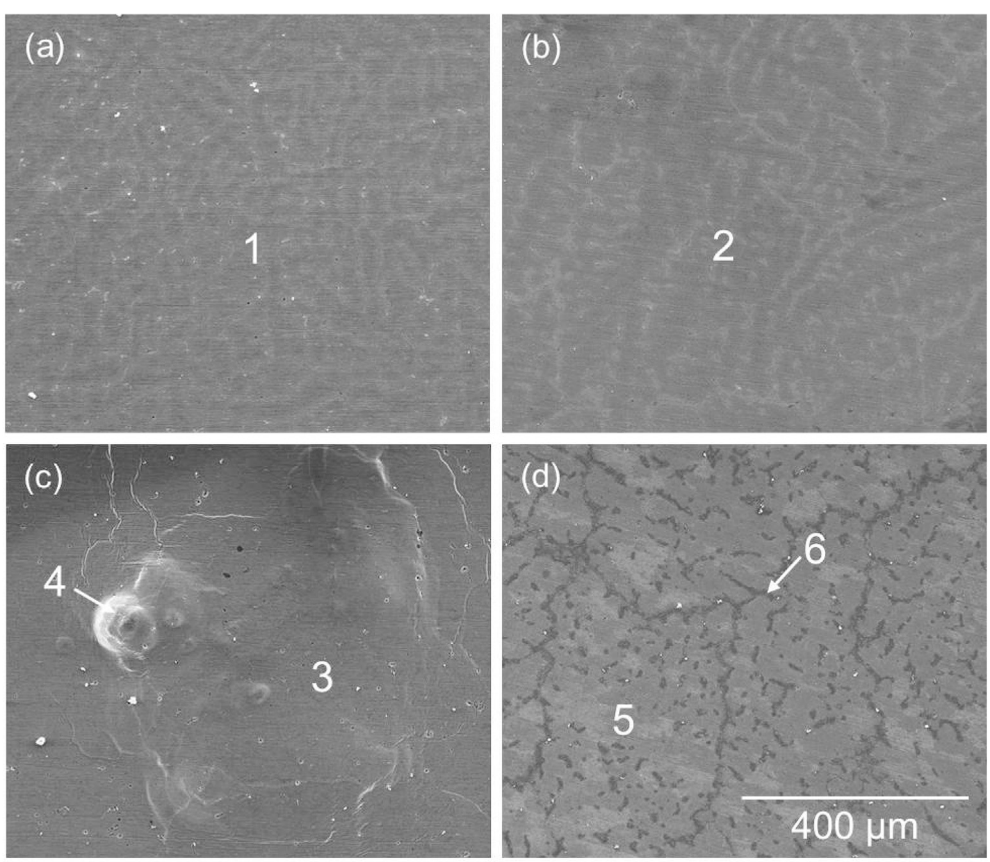

Fig. 2. SEM images of the surfaces oxidized for 72 h with the marks of analyzed regions. (a) Al-5 mass% Mg at 400 °C, (b) Al-5 mass% Mg-0.3 mass% Ca at 400 °C, (c) Al-5 mass% Mg at 500 °C and (d) Al-5 mass% Mg-0.3 mass% Ca at 500 °C.