This study focused on clarifying the effect of SiO₂ surface dopants on the formation of Al₂O₃/aluminum composites, especially on oxidation phenomena during the incubation period. The present results showed that a surface dopant decreased the incubation period of an Al-Mg-Si alloy, as well as that of an Al-Mg alloy, and that addition of an external surface dopant decreased the incubation period more effectively than did an internal alloying of silicon. A two-step oxidation process was also conducted. In the first step of the process, an aluminum alloy was oxidized without a surface dopant and cooled to room temperature during the incubation stage. In the second step, the same specimen was surface-doped with SiO₂ powder and reoxidized. The incubation time for the specimen subjected to the two-step oxidation process was the same as that for the single-step specimen oxidized with a surface dopant. The substantial decrease in the incubation period, especially for the Al-Mg-Si alloy, is ascribed to interaction surface dopant. The substantial decrease in the incubation period was the same as that for the single-step specimen oxidized with a surface dopant. The substantial decrease in the incubation period, especially for the Al-Mg-Si alloy, is ascribed to interaction surface dopant. The present study focused on clarifying the effect of SiO₂ surface dopants on the formation of Al₂O₃/aluminum composites, especially on oxidation phenomena during the incubation period.

I. Introduction

The primary disadvantage of ceramics for most structural applications is lack of reliability. This low reliability originates from low fracture toughness and brittle fracture behavior, which renders ceramics sensitive to sudden catastrophic failure in response to accidental overloading, contact damage, or rapid temperature changes. Many studies have been conducted on ceramic composites in an effort to enhance ceramic reliability without significant loss of other desirable properties.¹–³

One of the most promising methods for producing ceramic composites is known as the directed metal oxidation process (DIMOX; Lanxide Corp., Newark, DE) for aluminum alloys.⁴–⁷ The Al₂O₃/aluminum oxidation reaction product initially forms on the surface of a molten aluminum alloy and then grows outward, with a continuous supply of the alloy at the reaction front, through metal channels formed in the oxidation product. This process has many advantages such as low cost and net or near-net shape formation without size and shape limitations. Moreover, the DIMOX process is capable of producing composites with particulate or fiber reinforcement for favorable structural properties.

Much research has been conducted on the growth phenomena associated with variations of alloy composition, atmosphere, and processing temperature.⁸–¹⁴ Product growth depends crucially on the existence of a dopant, and such a dopant can be added to the parent metal internally, as an alloying element, or externally, in the form of an oxide powder on the top surface. Efforts have been made to elucidate the role of dopants.

Magnesium-free aluminum alloys containing silicon and zinc initiated directed oxidation growth as long as the molten alloy is in contact with bulk spinel (MgAl₂O₄).⁴ In the case of an aluminum alloy doped with magnesium only, Al₂O₃/aluminum composites were produced after removal of the scale that had formed during heating, but a long incubation period (~30 h) was necessary.¹² Mechanical disruption of the surface oxide on an aluminum alloy led to preferential-growth nucleation along the scratch,¹³ and an Al₂O₃/aluminum composite could be formed from an Al–1-wt%-Mg alloy with a minimum incubation period.¹⁴ On the other hand, a directed oxidation reaction can be induced by surface doping onto a pure aluminum metal or aluminum alloy surface. An Al₂O₃/aluminum composite has been grown from a powder compaction of aluminum and tin coated with MgO powder,¹⁵ or from a pure aluminum metal surface-doped with NaOH,¹⁶ or a lithium source,¹⁷ in the absence of any other dopants. However, few reports mention the formation of thick, uniform composites through the use of a surface dopant only.

Consistent reports have revealed that a SiO₂ surface dopant used during the directed oxidation reaction of an aluminum-based alloy induced the practical elimination of the incubation period and a uniform growth front.¹³,¹⁸–²⁰ Our preliminary experiments confirmed that SiO₂ is one of the most effective surface dopants for Al-Mg-based alloys. This effectiveness of SiO₂ may be important in actual application, because the oxidation reaction in such a case becomes predictable and controllable. The detailed mechanism of the effect produced by a SiO₂ dopant is unclear, even though several models have been proposed for the incubation mechanism. The present study focused on clarifying the effect of SiO₂ surface dopants on the formation of Al₂O₃/aluminum composites, especially on oxidation phenomena during the incubation period.

II. Experimental Procedure

To investigate the effects of SiO₂ surface dopants on the directed oxidation reaction of a molten aluminum alloy, four alloys of nominal compositions Al–(1,3,5)-Mg and Al–3Mg–5Si (in wt%) were prepared; those specimens are designated 1M, 3M, 5M, and 3M5S, respectively. Samples doped with SiO₂ powder on the alloy surface are designated D-3M or D-3M5S (where “D” refers to SiO₂ surface doping). The purities of the starting materials used in the present experiment were 99.9 wt% for the aluminum, 99.99 wt% for the magnesium, and 99.999 wt% for the silicon. All the alloys were prepared by induction melting, cast into cylindrical rods (~30 mm in diameter) using a graphite mold, and subsequently homogenized in air at 400°C for 10 h. The rods were...
machined into an appropriate cylindrical shape (6 mm in diameter × 5 mm long). The surfaces of the specimens were polished on 1000-grit SiC paper and ultrasonically cleaned in ethanol. The polished surfaces were coated evenly with a thin SiO₂ layer, for which the amount of SiO₂ powder varied within the range of 0.7–40 mg/cm². To achieve a uniformly coated layer, a suspension of SiO₂ powder (0.8 μm, High Purity Chemicals Laboratory, Sakato, Japan) was ultrasonically prepared with ethanol, dropped onto each specimen, and dried in air. For some experiments, specimens without a SiO₂ dopant were oxidized.

The oxidation experiments were conducted using a thermobalance (Model TG 92–18, SÉTERAM Scientific and Industrial Equipment, Caluire, France). Doped or undoped samples were placed in high-purity Al₂O₃ crucibles (7 mm inner diameter × 20 mm high) and heated at a rate of 20°C/min under a constant air flow of 417 mm³/s at standard temperature and pressure. Several experiments were interrupted at different stages to investigate the oxidized phases and the role of the SiO₂ surface dopant. Bulk-growth oxidation was conducted primarily at 1200°C.

Microstructures from selected stages of composite growth were examined using optical microscopy, SEM, and XRD. Energy-dispersive spectroscopy (EDS) and wavelength-dispersive spectroscopy (WDS) analyses were conducted for elemental analysis. With the aid of phase identification by XRD, EDS was helpful in identifying the chemical composition and phase distribution or sequence of layers in the surface oxide. For the chemical composition of thin surface oxide layers, point-spectra of EDS analyses were obtained at a constant electron voltage of 15 kV. The obtained X-ray intensities of the elements were compared with an EDS database and finally converted into atomic ratio through ZAF (atomic number-absorbance-fluorescence) collection factor. WDS analysis, which gives more quantitative information than EDS analysis, was conducted in a limited number of specimens.

III. Results

To investigate the effect of an SiO₂ dopant on the directed melt oxidation of an aluminum alloy, specimens were oxidized in a thermogravimetric (TG) apparatus. As reported previously,¹² the overall weight variation, as a function of process time, was composed of three steps: initial oxidation, resulting in the formation of surface oxide layers, an incubation period with limited weight gain, and bulk-growth oxidation, resulting in the formation of an Al₂O₃/aluminum composite. The incubation period is defined as the time from the end of initial oxidation to the start of bulk oxidation. Weight variations were strongly influenced by the presence or absence of a SiO₂ surface dopant and the alloy composition.

Figure 1 shows the oxidation behavior of Al-Mg and Al-Mg-Si alloys in the presence of a SiO₂ surface dopant. The incubation period of the Al-Mg alloy ranged from a few hours to several tens of hours, whereas the specimens containing silicon, added as an internal dopant (an alloying element) or an external dopant (a SiO₂ surface dopant), exhibited a significantly shorter incubation period. A decrease in the incubation period for doped samples was observed in both the Al-Mg-Si system and the Al-Mg system, indicating that the surface dopant did cause a decrease in the incubation period, even when silicon was included in the specimen as an alloying element. The shortest incubation period was for the D-3MSS specimen. A comparison of the incubation periods for D-3M and D-3MSS samples revealed that the incubation period of the D-3M sample was shorter. This result implies that external doping with SiO₂ was more effective than silicon alloying for decreasing the incubation period.

Figure 2 shows the effect of aluminum content on the incubation period in an Al-Mg alloy surface-doped with SiO₂ powder. The incubation period tended to increase with magnesium content, and this increase appears to be related to the amount of surface oxide layers (MgO-covered MgAl₂O₄) formed at the initial oxidation stage.

Figure 3(a) shows that the onset point of initial oxidation, which occurred at ~1000°C during heating, was independent of magnesium content in the aluminum alloy, but that the absolute value of weight gained at the initial oxidation increased as the magnesium content increased. However, the SiO₂ surface dopant did not significantly affect the initial oxidation, as shown in Fig. 3(b).

The strong effect of the SiO₂ surface dopant is well-depicted in Fig. 4. Even though only a small quantity of the SiO₂ powder (0.72 mg/cm²), corresponding to 0.02 wt% silicon dissolved in the aluminum alloy, was doped onto the alloy surface, the specimen exhibited almost the same incubation period. As shown in Fig. 1, only the magnesium-doped alloy (the Al-Mg alloy) lacked a consistent incubation time, whereas the other alloys, whether externally or internally doped with silicon, showed a reproducible incubation period. This result indicates that silicon is not necessary for composite growth, but rather seems to act as a promoter of composite growth, as pointed out previously.¹³

The elemental distributions of the D-3M and 3MSS specimens (Fig. 5) well-depict the sequence of oxide layers. According to X-ray data, the surface oxide layers of D-3M and 3MSS consisted only of MgO and MgAl₂O₄. From EDS analysis, magnesium and silicon were detected in the brightest region of Fig. 5(c), and only magnesium was detected in the brightest region of Fig. 5(g). Also, the magnesium:aluminum ratio in the intermediate region was 2:1. These results indicate that both specimens have a similar microstructure composed of a duplex (MgO-covered MgAl₂O₄) oxide layer. However, a high concentration of silicon was present in the MgO layer formed from the D-3M alloy (Fig. 5(d)), whereas no
detectable silicon concentration was present in the MgO layer formed from the 3M5S alloy without a dopant (Fig. 5(h)). No silicon was detected by WDS analysis in the MgAl2O4 layer of either specimen. An elemental line profile revealed that the silicon concentration in the MgO layer of the D-3M sample tended to decrease toward the metal reservoir, and that the SiO2 surface dopant disappeared during the last stage of the incubation period or the early stage of bulk-growth oxidation. After the bulk-growth oxidation, the surface oxide layers were composed only of MgO and MgAl2O4, according to the X-ray analysis. All these observations imply that the SiO2 surface dopant had dissolved into the molten alloy through the MgO layer. Moreover, a high concentration of aluminum was found in the nodules shown in Fig. 5(b), implying that metal microchannels appear to have already evolved in the MgAl2O4 layer in the incubation period.

A different type of experiment was conducted to examine the relationship between SiO2 doping and the incubation period (Fig. 6). The 3M specimen (with no SiO2 dopant) was heated to 1200°C, held for 1 h, and cooled to room temperature, a process corresponding to the earlier part of the TG curve, designated as the first heating. Then, the SiO2 powder was doped onto the surface of the specimen, and the specimen was reheated to 1200°C, according to the same heating schedule used for the first heating; this treatment was designated as the second heating.
incubation period. Most likely, the dissolution of the SiO2 dopant into the molten aluminum alloy through the MgO layer during the first heating, had already experienced enough of an incubation period to have evolved a duplex surface oxide layer (MgO-covered MgAl2O4) layer, but the dopant dissolves into the molten aluminum alloy through the MgO layer. The specimen shown in Fig. 6, after the first heating, had already experienced enough of an incubation period, ~60 min after initial oxidation, regardless of the SiO2 doping sequence. This finding implies that the incubation period is closely related to the MgO layer, which is the outermost oxide layer.

Figure 7 shows the bulk-growth rates of the specimens containing silicon in the form of either an internal or an external dopant. Data on the growth rate of the Al-Mg alloy without silicon was difficult to obtain because of the irregular reaction surface. All the growth rates reported here were obtained within the region of the planar front and constant growth rate. The growth rate and the apparent activation energy show almost the same values, irrespective of the alloy composition and the presence or absence of an SiO2 dopant. These results indicate that the silicon concentration in an aluminum alloy has no significant effect on the growth rate of the bulk Al2O3/aluminum composite.

IV. Discussion

The present experimental observations reveal that the decrease in the incubation period caused by the surface dopant is closely related to the interaction between the surface dopant and the outermost oxide layer (MgO layer). At the initial oxidation stage, the surface dopant has no significant effect on the formation of the duplex oxide (MgO and MgAl2O4) layer, but the dopant dissolves into the molten aluminum alloy through the MgO layer during the incubation period. Most likely, the dissolution of the SiO2 dopant proceeds by the solid-solution process. SiO2 is reported elsewhere to be up to 7wt% soluble in MgO at 1600°C. Although this temperature is higher than that used in the present experiment, SiO2 is considered to be soluble in an aluminum alloy through the MgO layer.

If the dissolved SiO2 releases silicon into the molten aluminum alloy, the effect of the released silicon would be about the same as with the internally alloyed silicon. Although the role of silicon is not clear, internally alloyed silicon is reported to increase the driving force for dissolution of the MgO layer into the molten aluminum alloy because of reduced magnesium activity, which results from the strong clustering tendency of magnesium and silicon atoms in the aluminum alloy. This clustering induces a thinner MgO layer, which provides favorable conditions for the formation of a bulk Al2O3/aluminum composite. Under such circumstances, the magnesium and oxygen from the dissolution of the MgO layer participate in the initiation of a bulk Al2O3/aluminum composite between the MgO and the MgAl2O4 layers, as reported by Antolin, Nagelberg, and others.

The magnesium migrates toward the outer surface of the MgO to form a new MgO layer, and the oxygen acts as an oxygen source for Al2O3 formation. However, because the incubation time of the D-3M alloy is shorter than that of the 3MSS alloy (Fig. 4), the dissolution process for the surface dopant through the MgO layer may have an additional effect on the MgO layer, as described by the following reactions:

\[
\text{SiO}_2(\text{MgO}) \rightarrow \text{Si}^{2+} + 2\text{O}_2 + 2\text{V}_{\text{mg}}^\circ
\]

The increased magnesium-vacancy concentration in the MgO layer increases the diffusivity of the released magnesium toward the MgO surface, as described in reactions (1) and (2), resulting in a decreased incubation period.

Two conditions must be satisfied for the formation of Al2O3/aluminum composites between the surface oxide layers:

1. a supply of aluminum alloy through the micrometal channel in the surface oxide layer (especially the spinel layer) must exist, and
2. an oxygen supply through the MgO layer must exist.

Therefore, the incubation period must depend on either the oxygen supply or the molten aluminum supply.

Previous theories for the incubation mechanism were based on the aluminum supply through the surface oxide layers. Salas et al. proposed that the initial rapid oxidation abruptly terminated with the formation of a dense spinel layer at the surface, leading to a long incubation period with limited weight gain. The proposed incubation mechanism is the process of metal-channel permeation into the dense spinel. Another report suggested that a SiO2 surface dopant reacts with an Al-Mg alloy and shortens the incubation period by providing sites in which the dense spinel layer that seals off the metal channels is prevented from forming. Antolin and Nagelberg theorized that the incubation period represents the thickening process of the MgO/MgAl2O4 duplex layer, and that the termination of the incubation period, bulk-growth initiation, is marked by the spread of the initiation front (a film of molten metal), originating from a flaw caused by the growth-induced stress.

In the present paper, we propose that the termination mechanism of the incubation period is related to the oxygen supply through the MgO layer. The specimen shown in Fig. 6, after the first heating, had already experienced enough of an incubation period to have evolved a duplex surface oxide layer (MgO-covered MgAl2O4) during the first heating. Thus, the SiO2 surface dopant on the second-heating specimen could only influence the MgO layer. Under these circumstances, if the incubation period is related to the molten aluminum supply, the SiO2 surface dopant on the second-heating specimen would not significantly decrease the incubation period.
incubation period. The oxygen supply needed to form the Al₂O₃/aluminum composite would be provided by the dissolution of the MgO layer, as proposed by Nagelberg et al. for the bulk-growth mechanism.

The growth rate of the composites supplements the dissolution of the MgO layer, as shown in Fig. 7. In the bulk-growth stage, the newly formed MgO layer is irrelevant to the MgO layer formed during the initial oxidation stage, in which the magnesium vacancies are formed by the solution of the SiO₂ dopant. Thus, the specimens undergoing bulk-growth oxidation should have similar MgO layers, regardless of the presence or absence of the SiO₂ surface dopant, and, thus, almost the same growth rate and apparent activation energy for bulk growth.

V. Conclusions

Addition of a SiO₂ surface dopant reduces the incubation period in Al-Mg-Si alloys, as well as in Al-Mg alloys. The substantial decrease in the incubation period, especially for the Al-Mg alloy, is ascribed to an interaction between the SiO₂ surface dopant and the MgO layer. During incubation, the dopant dissolves into the molten aluminum alloy through the MgO layer. This process makes the MgO layer thinner and can increase the number of magnesium vacancies in the MgO layer, thus providing the MgO layer with an appropriate microstructure for bulk-growth initiation.

The termination of the incubation mechanism is related to the oxygen supply through the MgO layer. The oxygen supply appears to be provided by the dissolution of the MgO layer into the molten aluminum alloy. This theory is supplemented by the fact that the composite growth rates and apparent activation energies for bulk growth show almost the same values in the specimens containing silicon as an alloying element or as an external surface dopant, because the newly formed MgO layer is independent of the existence of the SiO₂ surface dopant during the bulk-growth stage.

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References


