EVOLUTION OF MICROSTRUCTURE IN OXIDATIVE GROWTH OF Al_2O_3/ Al ALLOY COMPOSITES①

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ABSTRACT The evolution of microstructure in the oxidative growth of Al_2O_3/ Al alloy composites was examined metallographically and analyzed by electron microprobe technique. The development of a nonprotective surface layer of MgO/ $MgAl_2O_4$ allowed the continuous formation of an Al_2O_3-matrix composite containing an interpenetrating network of metal microchannels at 1 373 K. The role of Mg in the composite growth process was discussed by means of the lg a_{O_2} - Y_{Mg} phase diagram assuming that local equilibrium was established at the phase boundaries.

Key words oxide layer Al_2O_3/ Al alloy composites oxygen activity

1 INTRODUCTION

Unreinforced Al_2O_3/ Al alloy composites produced by the directed oxidation of molten Al alloys have been studied with respect to processing[1] and microstructure and properties[2-5]. In the compositing process, a molten aluminum with suitable alloying additions undergoes oxidation reactions and yields a continuous Al_2O_3 matrix with an interpenetrating three-dimensional network of Al alloy microchannels. The growth of the ceramic/ metal composites occurs continuously away from the melt surface while fresh alloy is supplied to the Al_2O_3/ Al alloy interface by fine microscopic channels through the oxide product. The final composites contains a continuous skeleton of Al_2O_3 phase and the residual metal in an interconnected matrix. The technology to produce these materials is quite flexible and offers the ability to make near-net-shape low-porosity in situ composites with a wide range of compositions and microstructures. These composites can, in principle, be designed to have good toughness and thermal shock resistance, as well as high stiffness, wear resistance and high-temperature stability.

This investigation examined the microstructure evolution in the oxidative growth of Al_2O_3/ Al alloy composites. This paper evaluated the role of Mg content on the conversion of the majority of the bulk Al into Al_2O_3 and described an investigation into the lg a_{O_2} - Y_{Mg} phase diagram. The first requirement for a systematic study of oxidation reactions to control Al_2O_3/ Al alloy microstructure is knowledge of phase equilibria, in particular, the effect of the oxygen activity. The small amount of previous research in this area is likely due to the existence of very few phase diagram displaying oxygen activity as a variable. It is believed that the basic scientific principles of controlling mirostructure can be established by work on log a_{O_2} - Y_{Mg} phase diagram.

2 EXPERIMENTAL PROCEDURE

The oxidation growth of molten Al alloy in air was studied by means of the interruption of the growth process at intermediate times during the isothermal soak. The aluminum alloy con-

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tained nominally 10% Si and 3% Mg. Up to four alloy samples were respectively placed in high purity Al_2O_3 crucibles and were simultaneously placed into a resistance heated box furnace and heated to an isothermal soak temperature of 1 373 K in air. Samples were removed one at a time and air-cooled after being held for various desired soak times (up to 48 h). The air-cooled specimens were cross-sectioned and metallographically mounted for microstructural examination. All samples were investigated using microscopy (Neophot 21) and electron microprobe analysis (X-650).

3 RESULTS

Fig. 1 shows the microstructure evolution of near-surface cross section of the oxide layers formed at 1 373 K on Al-3% Mg-10% Si alloy. After 5 h at 1 373 K, the alloy surface was covered with a duplex oxide scale consisting of an external dark layer (8.0 to 12 μm) on a gray layer (~ 40 μm). This duplex surface oxide structure is shown in Fig. 1(a). Energy dispersive X-ray analysis indicated an Al∶Mg ratio of 2∶1 in gray layer and only Mg in dark layer, suggesting that the gray and dark layers correspond to $MgAl_2O_4$ and MgO, respectively.

Fig. 1(b) shows that the thickness of the $MgAl_2O_4$ layer increased distinctly after 15 h at 1 373 K. Energy dispersive X-ray analysis showed that the $MgAl_2O_4$ layer contains metal microchannels developing from the bottom, which become progressively finer with distance

Fig. 1 Optical micrographs showing the microstructural evolution of near-surface cross section of the oxide layers on Al-3% Mg-10% Si alloy held at 1 373 K: (a) —5 h, (b) —15 h, (c) —25 h and (d) —48 h

from the $MgAl_2O_4$/Al alloy interface. The oxide nodules between the MgO and the $MgAl_2O_4$ layers were found and the external MgO layer formed initially was separated from the $MgAl_2O_4$ layer by these oxide nodules. Fig. 2 shows the corresponding X-ray maps for aluminum, magnesium and oxygen, revealing high concentrations of aluminum and oxygen within an oxide nodule, indicative of the presence of Al_2O_3. On the other hand, the strong magnesium signal on the undulated region of the oxide nodule surface indicates that the oxide nodule is covered with a thin layer of MgO. The strong Al signal adjacent to the MgO layer whithin the oxide nodule indicates that the oxide nodule consists of Al_2O_3 and aluminum and the aluminum microchannel appears to have reached the surface of MgO layer.

Bulk oxide growth follows the formation of the Al_2O_3/Al composite nodules. Fig. 1 (c) shows the microstructure of the surface oxide layers after 25 h at 1 373 K, Al_2O_3/Al alloy composite nodules grew and coalesced until a continuous composite layer of Al_2O_3 and Al alloy was formed between the external MgO layer and the innermost $MgAl_2O_4$ layer. Fig. 3 shows the scanning electron micrographs of the cross-section of the surface oxide scale in Fig. 1 (c) and the distributions of each element found by electron probe microanalysis (EPMA). The oxide scale was basically composed of three layers. Examination of EPMA taken at the different layers indicates that magnesium concentration is the highest in the outermost layer, the oxygen concentration is increased and the magnesium is not distributed in the next layer. Whereas the magnesium concentration increases abruptly and oxygen concentration distinctly dereases in the innermost layer. The results of EPMA analysis in conjunction with the energy dispersive X-ray analysis of the surface oxide structure indicate that the outermost scale layer is MgO, the intermediate one is Al_2O_3/Al alloy composite layer and the innermost $MgAl_2O_4$ and aluminum. In the Al alloy melt the oxygen concentration is higher. It is worthwhile mentioning that the EPMA examination indicates a silicon-enriched Al_2O_3/Al composite layer.

Fig. 2 Alumina nodule nucleating between the $MgAl_2O_4$ layers held at 1 373 K for 15 h, and the orresponding Al, Mg(and (O)) X-ray maps

Fig. 1(d) shows the microstructure of the Al_2O_3/Al alloy composites after 48 h at 1 373 K. The continued growth of the Al_2O_3/metal composite resulted in a product consisting of three dimensionally interconnected Al_2O_3 and metal networks, the gray region corresponds to Al_2O_3 phase and elemental silicon which precipitates from the molten alloy during cooling, the bright phase is aluminum containing small amounts of silicon and magnesium and the dark region is pores.

4 DISCUSSION

Phase diagram displaying the logarithm of the oxygen activity *vs* magnesium fraction at 1 373 K is very useful for selecting appropriate thermodynamic conditions in the oxidative growth of Al_2O_3/Al alloy composites. Fig. 4 shows a schematic lg a_{O_2}- Y_{Mg} phase diagram obtained by replotting the information contained in the isothermal section of the Al-Mg-O system

Fig. 3 Scanning electron micrographs of the cross-section of the surface oxide scale in Fig. 1 (c) and the distributions of each element found by EPMA

Fig. 4 Log a_{O_2} *vs.* magnesium fraction phase diagram at 1 373 K

at 1 373 K[6], where $a_{O_2} = p_{O_2}/p^\circ$ with $p^\circ = 1 \times 10^5$ Pa and $Y_{Mg} = n_{Mg}/(n_{Al} + n_{Mg})$. It is seen that the liquid (Al, Mg) with 3% Mg is in equilibrium with $MgAl_2O_4$ at very low lg a_{O_2}. At 1 373 K, the molten Al alloy surface rapidly oxidized to form a duplex surface scale consisting of a $MgAl_2O_4$ layer covered by a thin layer of MgO. Since the MgO found at the external surface is not a thermodynamically stable oxide for the range of alloy composition, its presence must be due solely to kinetic reasons. Formation of MgO phase involves the vaporization of Mg with high vapor pressure from the melt at the MgO/ Al alloy interface, permeation of Mg through the MgO layer, and reaction with oxygen at the MgO/ gas interface to form metastable MgO layer. Whereas the mobility of the Mg in $MgAl_2O_4$ is greater than that of Al[7, 8], Mg can easily become enriched, in the presence of an oxigen activity gradient, at the external surface of $MgAl_2O_4$ layer (on the side of higher activity) and eventually lead to the formation of an external MgO phase.

The interesting feature of the formation of the Al_2O_3/ metal was the early transition from the formation of $MgAl_2O_4$ to the formation of Al_2O_3 at the reaction front. Fig. 4 shows that the three-phase equilibrium of Al_2O_3+ liquid(Al, Mg) + $MgAl_2O_4$ is established at lg $a_{O_2} = -31.391$, one defines the content of 0. 40% Mg in liquid(Al, Mg) at 1373 K. The threshold Mg concentration in the liquid (Al, Mg) below which Al_2O_3 was expected to form instead of $MgAl_2O_4$ was determined to be 0. 40% Mg at 1 373 K . The Mg concentration would be reduced as the liquid(Al, Mg) with 3% Mg "wicks" up the microchannels in the $MgAl_2O_4$ layer, because the conversion of the liquid (Al, Mg) to $MgAl_2O_4$ causes the consumption of Mg in the microchannels. The formation of $MgAl_2O_4$ requires one Mg atom for every two Al atoms.

Since the alloy content is significantly less than this 1∶2 ratio, the continued formation of $MgAl_2O_4$ would locally deplete the alloy of Mg at the reaction interface. Once the Mg concentration dropped below the threshold level, Al_2O_3 would be formed instead of $MgAl_2O_4$. Fig. 4 shows that an extremely large oxygen activity gradient exists across the external MgO layer, it drove oxygen diffusion and dissolution in the liquid(Al, Mg) of the microchannels[5, 9]. At the Al_2O_3/Al alloy interface, the dissolved oxygen reacts with aluminum from the melt to extend the microchannels. The MgO layer, which is highly microcrystalline[9], controlled the supply of oxygen to the Al_2O_3/Al alloy interface. It is one of the causes that nodules of Al_2O_3/metal nucleuses were formed along the MgO/$MgAl_2O_4$ interface, Fig. 1(b). The composite growth reaction is sustainned by the wick action of liquid (Al, Mg) along interconnected microscopic channels within the alumina structure. Fig. 4 shows that the Al_2O_3 phase is in equilibrium with the liquid(Al, Mg) phase, as lg a_{O_2} is below -31.391 at 1373K. It is seen that increasing the oxidation time causes an increase in the amount of Al_2O_3 phase. The influence of the oxidation time is manifested through the diffusion of matter. The longer the oxidation time, the closer the Al_2O_3 to equilibrium with the liquid(Al, Mg). The Al_2O_3 content in the Al_2O_3/Al alloy composite increases and eventually results in a product consisting of three dimensionally interconnected Al_2O_3 and Al alloy networks.

The evolution of microstructure observed clearly demonstrates the necessity of carefully controlling the oxygen activity, Mg composition of Al alloy, and oxidation time to obtain certain desired Al_2O_3/Al alloy composites.

5 CONCLUSIONS

The growth of an Al_2O_3/Al alloy composites by the direct oxidation of molten Al-Mg-Si alloy was found to proceed through four distinct stages. First, during an isothermal soak of 1373 K, the molten alloy surface rapidly oxidized to form a duplex oxide layer consisting of an external MgO layer covering a layer of $MgAl_2O_4$ with interspersed metal. Second, during subsequent holding at 1373K, $MgAl_2O_4$ layer thickened and Al_2O_3/Al alloy composite nodules nucleated along the MgO/$MgAl_2O_4$ interface. Third, Al_2O_3/Al alloy composite nodules grew and coalesced until a continuous Al_2O_3/metal composite layer was formed. Finally, the Al_2O_3/metal composite layer cotinuously grew and eventually evolved into an Al_2O_3/Al alloy composites.

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