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Formation of aluminum/alumina ceramic matrix composite by oxidizing an Al–Si–Mg alloy

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Abstract

In the formation of an Al–Al_2O_3 ceramic matrix composite by oxidizing an Al–Si–Mg alloy, it was found from electron microscopy that MgO appeared first on the surface of the sample and followed by the formation of $MgAl_2O_4$ spinel. This order of appearance could be postulated by considering the high partial pressure of Mg and the Gibbs free energy associated with each reaction during annealing. The MgO inhibited the oxidation of molten Al underneath and preserved the Al metal inclusions, while spinel allowed oxygen to diffuse into the Al alloy so that Al was oxidized to form the Al_2O_3 ceramic matrix.

Keywords: Alloy; Al_2O_3–Al; Composites; Microstructure-final; Reaction sequence

1. Introduction

When aluminum is heat-treated in air, its oxidized surface hinders the further oxidation of the material. In the directed metal oxidation (DMO) method which was developed by the Lanxide Corporation,[1,2] Al–Al_2O_3 ceramic matrix composite (CMC) could be produced from oxidation of molten Al. In DMO, the oxide layer was made permeable to oxygen with appropriate dopant such as magnesium (Mg).[3–5] It was proposed that the production of Al–Al_2O_3 CMC first involved the formation of MgO surface layer then the $MgAl_2O_4$ spinel phase, and the production of Al_2O_3 was due to the decomposition of $MgAl_2O_4$.[3] However such model had not given an account for the formation of Al inclusions in the ceramic matrix of the composite. In this paper, we report our investigation on the microstructural development of the Al–Al_2O_3 composite during the oxidation of molten Al–Si–Mg alloy. The mechanism for the formation of such composite will be presented.

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2. Experiments and results

Aluminum cubes of 1 cm^3 contained 7.1 wt.% Si, 0.40 wt.% Mg, 0.14 wt.% Fe and 0.11 wt.% Ti were annealed in the furnace at 1000°C for 1, 3 or 6 h. The annealed samples were examined by scanning electron microscope (SEM). Elemental and compositional analyses were performed by energy dispersive X-ray spectroscopy (EDX). Some of the oxidized samples were leached by NaOH solution in order to dissolve the residual Al metal, so that the interfacial region between the metal inclusions and the ceramic matrix of the composite were revealed.

In the SEM study, we found that samples annealed for less than 3 h were covered with 2 μm needle-like crystals as shown in Fig. 1. The EDX analysis indicated that Mg was the sole detectable element on the surface, thus these needles were likely to be MgO crystals. Such observation was consistent with those previously reported.[6] As for those samples annealed for 6 h, some lump-like features and needles were found simultaneously on the surface as shown in Fig. 2. The analysis on these lumps indicated that they were $MgAl_2O_4$ spinel. The results of the analysis are tabulated in Table 1.

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In the study of interfacial regions between the freshly formed Al_2O_3 ceramic matrix and the residual Al metal, some octahedral spinel crystals of various sizes up to 2.5 μm were observed attaching to the composite body as shown in Fig. 3. The size of the Al inclusions in a bisected composite sample was also examined, it was found that they had irregular shape and some of them were interconnected. Their average size was about 3 μm (Fig. 4). Although the content of Si was larger than that of Mg, it had not been detected on the surface of the annealed product.

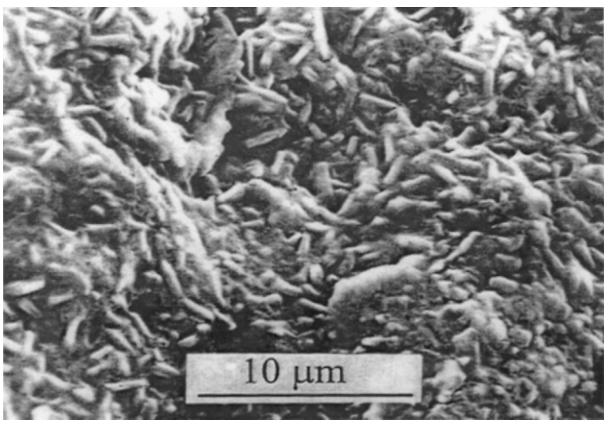

Fig. 1. SEM micrograph shows the MgO needle-like crystals formed on the surface of the sample after 3 h of annealing at 1000°C.

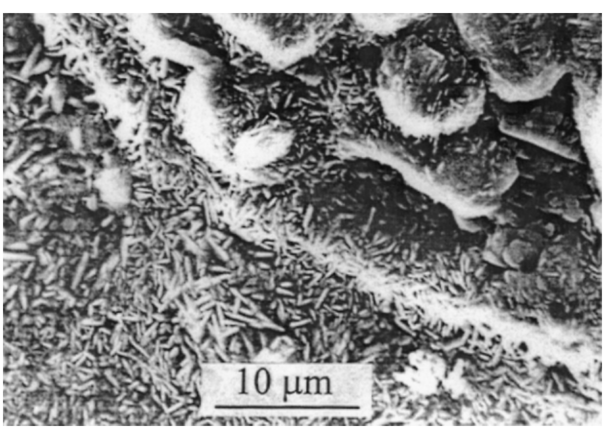

Fig. 2. SEM micrograph shows the surface of the sample annealed at 1000°C for 6 h. The surface contained the MgO needle-like crystals and the lumps covered with $MgAl_2O_4$ spinel.

Table 1
Compositions of Mg and Al in samples annealed at 1000°C for 1–6 h

Oxidation time (h)	Mg (at.%)	Al (at.%)	Si (at.%)	Phases	Remarks
1	100	0	0	MgO	Uniformly distributed
3	100	0	0	MgO	Uniformly distributed
	100±10	±10	0	MgO	At locations without lumps
6	82	18	0	Rich MgO and spinel	At locations with lumps
	58	42	0	MgO and spinel	
	10	90	0	Spinel + Al–Al_2O_3	

3. Thermodynamics of reactions

It was suggested that the cracks on the surface of the Al alloy had enhanced oxygen transport in DMO.[7] We had not observed surface cracks in our samples, the above postulate was therefore not applicable in this case. In order to provide an appropriate description for the oxidizing process of molten Al in the formation of Al–Al_2O_3 CMC, we had postulated the possible reactions during annealing, and calculated their corresponding Standard Gibbs free energies ΔG^o and the Gibbs free energies ΔG in each reaction at the annealing temperature 1000°C. The results are listed in Table 2. As an example, the calculation of $\Delta G^o_{1000^\circ C}$ and $\Delta G_{1000^\circ C}$ (in Joule per reaction when 1 mol of oxygen is used) in the formation of MgO are as follows:[8]

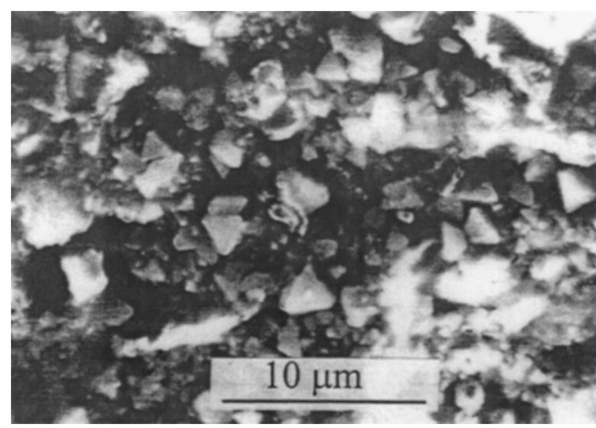

Fig. 3. SEM micrograph shows the octahedral spinel crystals (the light color grains) on the surface of the ceramic matrix (the dark background). The Al had been etched away by the NaOH solution so that the insoluble ceramics could be revealed.

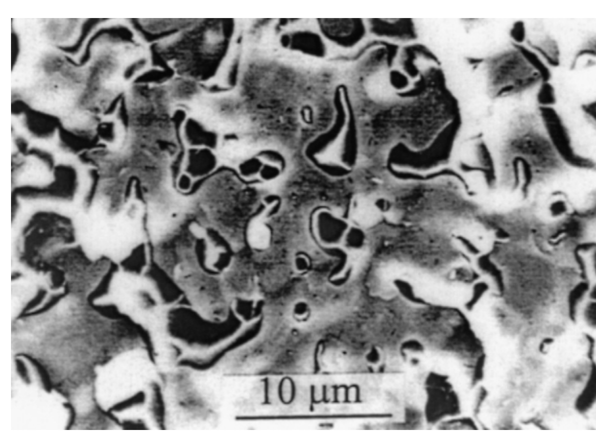

Fig. 4. SEM micrograph of the microstructure of cross-section of a sample annealed at 1000°C for 6 h. The Al inclusions had irregular shape embedded into the Al_2O_3 ceramic matrix.

Table 2
The possible chemical reactions during annealing and their corresponding standard Gibbs free energy $\Delta G^o_{1000^\circ C}$ and Gibbs free energy $\Delta G_{1000^\circ C}$ (*J* per reaction) at 1000°C

	Reaction	ΔG° (*T*) *J*/reaction	$\Delta G^o_{1000^\circ C}$ *J*/reaction	$\Delta G_{1000^\circ C}$ *J*/reaction
1	$2Mg + O_2(g) = 2MgO$	−1,219,140 + 233.04 *T*	−922,480	−789,079
2	$\frac{1}{2}Mg + Al + O_2(g) = \frac{1}{2}MgAl_2O_4$	−1,164,035 + 218.84 *T*	−885,451	−838,858
3	$\frac{4}{3}Al + O_2(g) = \frac{2}{3}Al_2O_3$	−1,121,922 + 215.47 *T*	−847,629	−829,972
4	$Si + O_2(g) = SiO_2$	−901,760 + 173.38 *T*	−681,047	−636,533
5	$MgO + Al_2O_3 = MgAl_2O_4$	−35,600−2.09 *T*	−38,261	–

$$\Delta G^o_{MgO} = -1{,}219{,}140 + 233.04T \quad (1)$$

and $\Delta G^o_{MgO} = -922{,}480 J$/reaction at $T = 1000°C$.

$$\Delta G_{MgO} = \Delta G^o_{MgO} - RT\ln\left(a^2_{Mg}\cdot P_{O_2}/P^o\right) \quad (2)$$

where a_{Mg} is the concentration of Mg and P_{O_2}/P^o is the partial pressure of oxygen. When a_{Mg} was 0.004 and $P_{O_2}/P^o$was 0.21, ΔG_{MgO} was equal to −789,079 *J*/reaction at $T = 1000°C$. As for the formation of $MgAl_2O_4$ and Al_2O_3, their corresponding Gibbs free energies at 1000°C can be found from the following equations:

$$\Delta G_{MgAl_2O_4} = \Delta G^o_{MgAl_2O_4} - RT\ln\left(a^{\frac{1}{2}}_{Mg}\cdot a_{Al}\cdot P_{O_2}/P^o\right) \quad (3)$$

and

$$\Delta G_{Al_2O_3} = \Delta G^o_{Al_2O_3} - RT\ln\left(a^{\frac{4}{3}}_{Al}\cdot P_{O_2}/P^o\right) \quad (4)$$

As listed in Table 2, the $\Delta G_{1000^\circ C}$ in the formation of MgO using 1 mol of O_2 was equal to −789,079 *J*, which was higher than those of $MgAl_2O_4$ (−838,858 *J*) and Al_2O_3 (−829,972 *J*). Therefore, $MgAl_2O_4$ would have formed first among the reactions involved during annealing. However, Mg has a relatively high standard vapor pressure P^o_{Mg} equal to 41.7 kPa, it is only 3.53×10^{-3} kPa for Al.[9] According to the Rault's law, the partial pressure of Mg and Al in this case would be:

$$P_{Mg} = P^o_{Mg}a_{Mg} = 41.7 \times 0.004 = 0.1668 \text{ kPa} \quad (5)$$

$$P_{Al} = P^o_{Al}a_{Al} = 0.00353 \times 0.9225 = 0.00326 \text{ kPa} \quad (6)$$

The mole fraction of Mg (a_{Mg}) in the gas phase was therefore equal to 0.981 even though its initial concentration in the alloy was only 0.4 wt.%, and the mole fraction of Al (a_{Al}) in the gas phase is 0.019. In the calculation of Gibbs free energy in the formation of MgO when $a_{Mg} = 0.981$ at 1000°C using the Eq. (2), $\Delta G_{Mgo} = -905{,}555$ *J*/reaction. As for the formation of $MgAl_2O_4$ and Al_2O_3 when $a_{Al} = 0.019$ at 1000°C, $\Delta G_{MgAl_2O_4} = -826{,}882$ *J*/reaction [from Eq. (3)] and $\Delta G_{Al_2O_3} = -755{,}178$ *J*/reaction [from Eq. (4)]. Therefore, the value of $\Delta G_{1000^\circ C}$ for forming MgO (−905,555 *J*) at the surface of this molten Al-based alloy was lower than those of forming $MgAl_2O_4$ and Al_2O_3. Based on the results of these calculations, the order of priority of the reactions was as follows: [reaction (1)] Mg was oxidized to MgO, [reaction (2)] Mg and Al were oxidized to $MgAl_2O_4$ spinel, [reaction (3)] Al was oxidized to Al_2O_3, and [reaction (4)] Si was oxidized to SiO_2. The $\Delta G^o_{1000^\circ C}$ of reaction between MgO and Al_2O_3 [reaction (5)] which formed $MgAl_2O_4$ was also listed in the table.

4. Model for the formation of CMC

4.1. Mechanism

Based on the above thermodynamic approach, our proposed mechanism in the formation of the Al-Al_2O_3 CMC is as follows. In the initial stage of annealing, MgO was formed on the surface of the Al–Si–Mg alloy via reaction (1), because Mg had higher partial pressure and higher affinity to oxygen than other ingredients in the alloy. The $\Delta G_{1000^\circ C}$ in the formation of MgO at the surface was −905,555 *J* which was the lowest among all the possible reactions in the oxidation of this alloy. Thus, the possibility of Al replacing Mg in the initial oxidation was highly improbable although such claim had been found in other models.[7] The high oxygen affinity of Mg had prevented the oxidation of molten Al to occur, therefore the time required to penetrate through or to replace this MgO surface layer was the incubation period for commencing the growth of Al_2O_3. In prolonged oxidation, the concentration of Mg decreased, and reaction (2) began, thus the incubation period also depended on the amount of Mg in the alloy. At this stage, the Mg–Al–O spinel was formed. The facts that spinel usually appeared as a solid solution[10] and possessed excessive cation vacancies (Mg^{2+}), the diffusion process of the O^{2-} ions would be enhanced. However, reaction (2) did not occur on the entire surface of the sample; certain locations were fully covered with spinel phase while other was still covered with thin MgO crystals. The oxidation of the molten Al continued as oxygen diffused through the $MgAl_2O_4$ spinel forming Al_2O_3, while those Al underneath MgO was prevented from oxidation. At this stage, the composite contained Al inclusions and an Al_2O_3 matrix. When the sample was further annealed, most of the MgO became part of the $MgAl_2O_4$ spinel after MgO had reacted with Al_2O_3 as described in reaction (5).

4.2. Microstructure of Al–Al_2O_3 CMC

The above description of the oxidation process was consistent with the results obtained from the SEM and EDX studies. The micrograph in Fig. 1 shows the surface of the sample annealed for 3 h on which only Mg was found, while micrograph in Fig. 2 showed the presence of both Mg and Al on the surface of the sample annealed for 6 h. (EDX was unable to resolve the presence of oxygen). In the oxidation of Al and the formation of Al_2O_3 underneath the spinel crystals, molten Al was able to spread out and filled the regions between the spinel crystals and the newly formed Al_2O_3 ceramic via the capillary action. The thin layer of molten Al was readily to be oxidized and solidified to form Al_2O_3 as part of the ceramic matrix which pushed the spinel and MgO outward forming the lump-like feature on the surface of the sample. While the MgO layer did not support oxygen diffusion thus protecting those Al underneath from oxidation and built up columns of molten Al located in between the newly formed Al_2O_3 matrix. Some of the spinel crystals were trapped at the interface of the grown Al_2O_3 and the molten Al, their presence had been revealed by SEM as shown in Fig. 3.

It was reported that when Pd[11] or Ni[12] was added onto the surface of Al, fine Al inclusions were produced in the alumina matrix. It was explained that Pd or Ni had introduced large number of nucleation sites for the formation of fine spinel grains, that enhanced the growth of the ceramic matrix by shortening the distance of oxygen diffusion from the surface to the molten Al where the aluminum oxide was formed. Thus, fine Al inclusions were found in those CMC which were covered with fine spinel grains. In our CMC sample, we observed that the dimension of the spinel grains was about 2.5 μm (Fig. 3), and the average size of the irregular Al inclusions was about 3.0 μm. This suggested that the size of these preserved Al inclusions might also be related to that of the spinel. During annealing, the octahedral spinel crystals were formed, and randomly but closely packed above the molten Al on the surface of the alloy. The regions between the individual spinel crystals had irregular shape but also had size in the same order of magnitude of the spinal crystal. In these regions, there were the needle-like MgO crystals that covered the rest of the alloy surface. The preserved Al inclusions which were underneath these MgO crystals thus found to have the same dimension (shown in Fig. 4) as those of the spinel crystals.

5. Conclusions

An Al–Si–Mg alloy with low Mg content had been fabricated into Al–Al_2O_3 ceramic matrix composite. The order of appearance of the possible reactions during annealing had been postulated on the basis of the partial pressure of Mg and Al, and the Gibbs free energy of individual reaction. Such order had been verified by the SEM and EDX studies. A model had also been proposed to describe the formation of this CMC. In the model, the presence of alternate oxygen diffusive and non-diffusive top layer was the crucial factor for the continuous oxidation of Al. The former was the MgO needle-like crystals formed on the surface in the initial stage of annealing, whereas the latter was the octahedral Mg–Al–O spinel crystals formed by the reaction between Al and Mg in the presence of oxygen. Based on this mechanism, the MgO regions preserved the Al inclusions underneath while the spinel allowed the continuous oxidation of molten Al to produce the Al–Al_2O_3 ceramic matrix composite.

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