Morphology of Spinel and Al_2O_3 Particles in an $\text{Al}_2\text{O}_3/\text{Al-Mg-Si}$ Composite Material Revealed by Scanning Low Energy Electron Microscopy

K. Matsuda¹, T. Matsuki^{2,*}, I. Müllerová³, L. Frank³ and S. Ikeno¹

¹Faculty of Engineering, University of Toyama, Toyama 930-8555, Japan

²Graduate School, University of Toyama, Toyama 930-8555, Japan

³Institute of Scientific Instruments, Academy of Sciences of the Czech Republic, Královopolská 147, CZ-61264, Brno, Czech Republic

In metal matrix composite materials consisting of oxide particles and Al alloys, including Mg as a solute atom, MgAl_2O_4 spinels are formed at the interface between the particles and the matrix. In the present study, the scanning low energy electron microscopy (SLEEM) method has been applied to confirm morphologies of $\alpha\text{-Al}_2\text{O}_3$ particles and MgAl_2O_4 spinel crystals grown on the alumina particles in the $\text{Al}_2\text{O}_3/\text{Al-1.0 mass\% Mg}_2\text{Si}$ alloy composite material. The morphology of $\alpha\text{-Al}_2\text{O}_3$ particles before fabrication of the composite material was like a faceted barrel with 2 hexagonal $\{0001\}$ and 6 trapezoidal $\{1101\}$ planes. Spinel was formed on facets of Al_2O_3 as small particles, and their shape was an octahedron consisting of 8 equiaxial triangles. Spinel and Al_2O_3 particles keep their orientation relationship which was concluded by our recent TEM study:

$$(111)_{\text{MgAl}_2\text{O}_4} // (0001)_{\text{Al}_2\text{O}_3}, \quad [2\bar{1}\bar{1}]_{\text{MgAl}_2\text{O}_4} // [2\bar{1}\bar{1}0]_{\text{Al}_2\text{O}_3}, \quad [1\bar{1}0]_{\text{MgAl}_2\text{O}_4} // [1\bar{1}00]_{\text{Al}_2\text{O}_3}$$

[doi:10.2320/matertrans.47.1815]

(Received March 13, 2006; Accepted May 1, 2006; Published July 15, 2006)

Keywords: scanning low energy electron microscopy, composite material, spinel, alumina, aluminum-magnesium-silicon alloy

1. Introduction

Metal matrix composites have been investigated by many researchers motivated by aims to add new properties to standard materials. For example, with respect to age-hardenable Al alloys, much improved heat resistance as well as wear resistance has been expected for engine parts of automobiles. Several types of composite materials exhibiting age-hardenability have been examined in our recent studies, and it has been clarified that in composites consisting of oxide particles and Al alloys, including Mg as a solute atom, spinels are formed at the interface between the particles and the matrix.¹⁻⁶⁾ In one of our studies, the orientation relationship between Al_2O_3 and MgAl_2O_4 (spinel) was investigated in TEM samples prepared by the FIB method, and the following results were obtained:⁷⁾

$$(111)_{\text{MgAl}_2\text{O}_4} // (0001)_{\text{Al}_2\text{O}_3}, \quad [2\bar{1}\bar{1}]_{\text{MgAl}_2\text{O}_4} // [2\bar{1}\bar{1}0]_{\text{Al}_2\text{O}_3}, \quad [1\bar{1}0]_{\text{MgAl}_2\text{O}_4} // [1\bar{1}00]_{\text{Al}_2\text{O}_3} \quad (1)$$

Further, the observed morphology of the spinels indicated that the spinel grows towards the Al_2O_3 particle. However, as the TEM method was used in this study, the morphology of the spinel could not be perceived in 3 dimensions.

The scanning low energy electron microscopy (SLEEM) method is a technique developed quite recently, and currently being disseminated into perspective fields of application. The contrast mechanisms relevant to slow electrons, the principles of the necessary instrumentation, and models enabling one to interpret various SLEEM images have been treated in many of Frank and Müllerová's works.⁸⁻¹⁰⁾ Owing to the greatly reduced penetration depth of low energy electrons,

the method obtains information quite near to the surface of specimens, and the free choice of the landing energy of electrons allows the method to be applied even to insulating materials. For our conventional SEM a special SLEEM detector was designed and assembled, and its performance has been demonstrated in our recent work on several samples.¹¹⁾

In this study, the SLEEM method has been applied to reveal the morphology of Al_2O_3 particles and MgAl_2O_4 spinel crystals, in order to contribute to the explanation of the formation mechanism of spinels.

2. Experimental

2.1 Samples

A billet of $\text{Al}_2\text{O}_3/\text{Al-1.0 mass\% Mg}_2\text{Si}$ alloy composite material was made by the method described in our recent reports.^{6,7)} In the present work we used high purity $\alpha\text{-Al}_2\text{O}_3$ particles of a mean diameter of about $1.5\text{ }\mu\text{m}$, provided by Sumitomo Chemical Co. Ltd. Samples for the scanning electron microscope (SEM) were prepared by the normal electrolytic polishing method, in which just the Al matrix was dissolved and particles were left intact on the surface. A mixture of ethanol and perchloric acid (9:1) was used for an electrolytic polishing, its temperature was kept about 253–263 K, and voltage during polishing was 10–20 V. In order to confirm the microstructure of the composite material, a transmission electron microscope (TEM) was also used at 200 kV.

2.2 The SLEEM method

The SLEEM detector and the necessary modifications to the specimen stage had been specially designed for our SEM.

*Present address: Aishin Keikinzoku, Co. Ltd., Imizu 934-8588, Japan

Fig. 1 Measured resolution of the SLEEM detector adopted on our SEM.

Table 1 Measured point resolution of our SLEEM detector.

Landing energy of electron	resolution
1000 eV	11.6 nm
300 eV	13.2 nm
100 eV	15.5 nm
30 eV	16.7 nm

The detector was manufactured at ISI Brno, while Hitachi Science Technology performed the stage modification. The energy of electrons landing on the samples is controlled by a negative potential applied to the sample. When, for example, the energy of primary electrons is 10 keV, and the sample is negatively biased to 9.9 keV, the landing energy of electrons on the specimen is only 0.1 keV. The SEM (Hitachi S3500H) has a normal tungsten filament and standard vacuum system with a diffusion pump. The measured image resolution in the SLEEM adaptation to Hitachi S3500H is shown in Fig. 1,

and has been discussed in our recent work.¹¹⁾ The best image resolution of the SEM itself is 4.5 nm at 30 keV. At 25 keV, the resolution of the secondary electron (SE) image is about 5.5 nm (Fig. 1). Below 1000 eV, objects sized between 10 and 20 nm can be clearly resolved in the SLEEM mode. When, for example, a resolution of 15 nm is required, the SLEEM mode uses electrons incident at about 100 eV, while the standard SEM mode needs not less than 10 keV. The measured resolution of the SLEEM mode at energies below 1000 eV is summarized in Table 1. A high performance, field-emission type SEM (FE-SEM) (JSM 6700F) at ISI ASCR, equipped with an energy dispersive X-ray spectroscopy (EDS), was also used to compare the micrographs.

3. Results and Discussion

3.1 TEM observation

Figure 2 shows a TEM image of the composite material aged at 473 K for 24 ks. We see the matrix with needle shaped precipitates and dark particles. The region X, located at the boundary between the Al_2O_3 particle and the matrix, was analyzed by EDS and shown to have a noticeable O peak along with Mg and Al peaks, see Fig. 2(b). Accordingly, this small particle was identified as MgAl_2O_4 , and similar small particles marked by arrows were also identified as spinels. The large particle marked by Y showed no traces of Mg in Fig. 2(c), so this was recognized as an Al_2O_3 particle. However, in this sample prepared by conventional electrolytic polishing, the morphology of the particles cannot be determined in more detail because of their thickness in the third dimension.

3.2 SLEEM work

Figure 3(a) shows a high magnification SLEEM image of the Al_2O_3 particles that were used to fabricate the composite. These particles were not coated with any conductive material for observation by SEM. Even so, the particles were clearly

Fig. 2 TEM study for the composite material aged at 473 K for 24 ks (a) a bright field TEM image, and (b) and (c) are EDS profiles obtained from positions marked by X and Y in (a).

Fig. 3 (a) a SLEEM image of Al₂O₃ particles before fabricating composite, and (b) its schematic morphology of α -Al₂O₃ particle.

visible along with their facets. These facets correspond to the calculated equilibrium morphology of an unhydrated α -Al₂O₃ crystal, reported by de Leeuw and Parker,⁹⁾ so in Fig. 3(a) they are indexed according to this work. Figure 3(b) then shows the schematic morphology of the α -Al₂O₃ particle according to our SLEEM observation. The α -Al₂O₃ particle typically resembles a faceted barrel with two hexagonal {0001} planes and 6 trapezoidal $\{\bar{1}101\}$ planes, although the prism-like $\{\bar{1}100\}$ or $\{11\bar{2}0\}$ planes were not observed frequently. As the {0001} plane on α -Al₂O₃ decreases the surface energy and increases the stability of the surface,¹²⁾ the used alumina particles can be considered quite stable.

Figure 4 shows the normal secondary electron (SE) and backscattered electron (BSE) images obtained from the composite material with 10 keV primary electrons. In the SE image in Fig. 4(a) some Al₂O₃ particles seem to be slightly charged up, and some quite fuzzy smaller particles can be seen on their surface. In the BSE image in Fig. 4(b), outlines of small and large particles as well as small ones can be seen, but no shape details are visible. According to Fig. 2, the small particles are thought to represent MgAl₂O₄ crystals, so hereinafter they are referred to as spinels. It is obvious that no detailed morphology of spinels is provided by SE and BSE images at 10 keV.

Figure 5 shows a SLEEM image taken with 10 keV primary electrons landing on the specimen surface with energy of 1 keV. Large Al₂O₃ particles with small spinels are significantly more visible than in the SE and BSE images in Fig. 4. The alumina particles show facets similar to those in Fig. 3(a), and the spinels can be identified as polygonal objects.

In Fig. 6, we see the spinels on Al₂O₃ observed by SLEEM at a higher magnification. The facets of the Al₂O₃ particle are

Fig. 4 SEM images obtained from the composite material by the primary electron of 10 keV. (a) SE and (b) BSE images.

near to the hexagonal {0001} and trapezoidal $\{\bar{1}101\}$ planes shown in Fig. 3(a). This means that the facets of the Al₂O₃ particles are very stable and do not change during the fabrication process of this composite material. This information was not available from our previous work. On the facets

Fig. 5 SLEEM image obtained from the same position as in Fig. 4 by primary electron of 10 keV.

of the Al_2O_3 particle there are many spinels marked by arrows, with a size of which is around 200 nm. Some spinels can even be observed 3-dimensionally—for example that marked by S exhibits an octahedral shape formed by 8 planes as shown in Fig. 6(b). This result is quite close to that reported by Wang and Zanzucchi¹³⁾ who stated the single crystal of MgAl_2O_4 having an octahedral shape was formed by 8 facets of (111) plane. In the present work the facets of spinels were also indexed as (111)—see Fig. 6(b). The micrograph in Fig. 6 indicates that the octahedrons are fixed in facets of Al_2O_3 particles. The octahedral spinel is likely to nucleate on a facet of the Al_2O_3 particle, which also forms an interface between Al_2O_3 and the Al-matrix, and then grows both into the matrix and the particle absorbing elements required to compose MgAl_2O_4 . According to our report using TEM,⁷⁾ the crystallographic orientation relationship between the spinel and Al_2O_3 is as described by eq. (1). Thus, it is

quite surprising that the (111) facets of the spinel, which should have a relationship with Al_2O_3 , are so visible in the SLEEM image in Fig. 6.

Figure 7 shows a SLEEM image of the spinels on the Al_2O_3 particle at higher magnification. The spinel marked A in Fig. 7(a), showing a diamond shape, is situated on the Al_2O_3 facet marked by B. SLEEM also confirmed a spinel, marked by the white arrow, which is smaller than 100 nm. When the facet marked H is assumed to be the (0001) plane of Al_2O_3 and the dotted double arrow is parallel to the $[\bar{1}\bar{1}2]$ direction of spinel, a 3-dimensional model, shown in Fig. 7(b), can be drawn according to the results in Figs. 3 and 6 and our recent TEM work. It is obvious from this figure that the $(111)_{\text{spinel}}$ plane is parallel to (0001) of Al_2O_3 , and that Fig. 7(a) shows a projection nearly parallel to both $[1\bar{1}0]_{\text{spinel}}$ and $[1\bar{1}00]_{\text{alumina}}$ directions. A similar relationship was confirmed by an HRTEM study of MgAl_2O_4 at the $\text{MgO}/\text{Al}_2\text{O}_3$ interface formed by MBE growth of MgO films on Al_2O_3 .¹⁴⁾

Naturally, three-dimensional information has not been obtained in our TEM studies, so only the combination of TEM and SLEEM techniques in this study has provided more accurate crystallographic information.

3.3 SLEEM in FE-SEM

By means of a feasible adaptation, the SLEEM imaging mode can be introduced into a variety of commercial SEM types, including high-resolution field-emission SEM (FE-SEM).¹⁰⁾ Figure 8 shows a SLEEM image obtained with an adapted FE-SEM at a 3 keV landing energy of electrons achieved with an 8 keV primary beam and -5 kV specimen bias. The microscope (JSM 6700F from JEOL) has a nominal resolution of 1 nm at 15 keV and 2.2 nm at 1 keV, while in the SLEEM mode 9 nm at 10 eV has been demonstrated at a working distance of 7.5 mm with the SLEEM detector inserted between the objective lens and the specimen.¹⁰⁾

The improved resolution of micrographs acquired with this

Fig. 6 (a) SLEEM image of spinels on Al_2O_3 in the composite material, and (b) a schematic illustration of spinel particle.

Fig. 7 (a) SLEEM image of the spinels on the Al₂O₃ particle in higher magnification, and (b) the explanation of orientation relationship between the spinel and Al₂O₃ particle.

Fig. 8 SLEEM image by FE-SEM.

device reveals more details of the morphology of particles. It is clear apparent that spinels come out from the facets of Al₂O₃ particles and do not grow on corners or ridges. Cao and Campbell reported the crystallographic orientation relationship between the Fe-rich phase and oxide films in Al–11.5 Si–0.4 Mg (mass%) cast alloy, and pointed out that the nucleation agent is potent if the planar disregistry is less than 12%.¹⁵⁾ We have considered some simpler pairs of lattice planes, which may concern the orientation relationship obtained in the present work, namely (111)_{spinel} and

Table 2 Lattice misfits between MgAl₂O₄ and Al₂O₃.

Lattice planes of MgAl ₂ O ₄	Lattice planes of Al ₂ O ₃	Calculated misfit
(111), 0.4668 nm	(0003), 0.4334 nm	7.2%
(448), 0.0825 nm	(3360), 0.0794 nm	3.8%
(440), 0.1430 nm	(3300), 0.1375 nm	3.8%

(0003)_{alumina}, (448)_{spinel} and (3360)_{alumina}, and (440)_{spinel} and (3300)_{alumina}. Their lattice misfits were calculated using eq. (2) and the results summarized in Table 2.

$$\text{misfit}_{(hkl)\text{spinel}}^{(hkl)\text{alumina}} [\%] = \left| \frac{d_{(hkl)\text{alumina}} - d_{(hkl)\text{spinel}}}{d_{(hkl)\text{spinel}}} \right| \times 100 \quad (2)$$

In eq. (2), $(hkl)_{\text{alumina}}$ and $(hkl)_{\text{spinel}}$ are the spacing of the (hkl) planes in alumina and the spinel, respectively. All values are lower than 10%, which also supports the given orientation relationship as that enabling easy nucleation of a spinel on the Al₂O₃ surface. According to Rossi and Fulrath,¹⁶⁾ the growth of a spinel on sapphire occurs by only a slight shift in the oxygen position and results in the same orientation relationship between the spinel and the sapphire as that mentioned above.

Figure 9(a) shows a SLEEM image of particles on the surface of a composite material. The EDS data were obtained at a landing energy of 3 keV, which can be considered narrowly sufficient for excitation of O, Mg, and Al-K α lines. The EDS spectra, acquired at the points marked A and B in Fig. 9(a) and shown in Fig. 9(c) and (d), exhibit high O and Al peaks in both positions, while the Mg peak is apparent only at point A. In the Mg-K map in Fig. 9(b), the white arrow points to the same spinel about 230 nm in size, which is marked with the black arrow in Fig. 9(a). In a similar way we have also verified the presence of Mg for other spinels on Al₂O₃ particles, as well as the absence of Mg at points located outside the spinels. This means that the Mg atoms needed for the growth of spinels are provided directly by the molten Al-based alloy, and do not come from any other reaction products such as MgO.³⁾ As each spinel was located in the center of a dimple on a facet of the Al₂O₃ particle, the reaction for the growth of spinels takes place just at the interface between Al₂O₃ and the molten metal during fabrication of this composite material.

Lu *et al.* identified a continuous layer made of small MgAl₂O₄ and Si particles in the mullite/Al–1.0 mass% Mg alloy composite material.²⁾ In the present study, the matrix alloy for the composite material was Al–1.0 mass% Mg₂Si alloy, which also contains Si atoms. However, none of the Si phase, Mg₂Si equilibrium phase or SiO₂ was detected at the interface between Al₂O₃ and the matrix. According to the present results and our previous studies,^{6,7)} during formation of this composite material under the given fabricating conditions Si atoms remain in the matrix as solute atoms. As no other oxides such as MgO, SiO₂, or other kinds of aluminum oxides were identified in this composite material, we can consider the molten Al as not containing any extra oxygen. From the above results, we can conclude that the reaction process to form spinels is as follows:

Fig. 9 Chemical analysis of particles. (a) SLEEM image, and (b) Mg-K map obtained from the same area of (a). (c) and (d) are EDS profiles detected from positions marked by A and B in (a).

4. Conclusions

Morphologies of α - Al_2O_3 particles and MgAl_2O_4 spinel crystals grown on the alumina particles in the $\text{Al}_2\text{O}_3/\text{Al}$ –1.0mass% Mg_2Si alloy composite material have been investigated by the SLEEM method. The following new facts were obtained:

- (1) The SLEEM method provided much better readable and detailed images of all particles, their shapes and mutual orientations, in comparison with conventional SE and BSE images at the electron energies usually used in the SEM. This is due to the much smaller interaction volume of signal exciting electrons in the target and hence more localized information, together with a favorable combination of secondary (SE) and back-scattered (BSE) electron signals.
- (2) The morphology of α - Al_2O_3 particles before fabrication of the composite material was like a faceted barrel with 2 hexagonal $\{0001\}$ and 6 trapezoidal $\{\bar{1}101\}$ planes. These facets were stable and preserved in the process of fabrication of the composite material.
- (3) Spinel was formed on facets of Al_2O_3 as small particles, and their shape corresponded well to an octahedron consisting of 8 equiaxial triangles.
- (4) By a combination of TEM and SLEEM techniques, the following crystallographic orientation relationship between spinels and Al_2O_3 was confirmed in 3 dimensions:

Acknowledgement

This study was supported by the Research Project 2003–2004 of the Venture Business Laboratory in the University of Toyama, Japan.

REFERENCES

- 1) H. Ribes, M. Suery, G. L'esperance and J. G. Legoux: *Met. Trans. A* **21** (1990) 2489–2496.
- 2) P. Lu, R. E. Loehman, K. G. Ewsuk and W. G. Fahrenholtz: *Acta Mater.* **47** (1999) 3099–3104.
- 3) B. Srinivasa Rao and V. Jayaram: *Acta Mater.* **49** (2001) 2373–2385.
- 4) Z. P. Luo, Y. G. Song and S. Q. Zhang: *Scripta Mater.* **45** (2001) 1183–1189.
- 5) A. Daoud and W. Reif: *J. Mater. Process. Tech.* **123** (2002) 313–318.
- 6) S. Ikeno, K. Matsuda, S. Rengakuji and Y. Uetani: *J. Mater. Sci.* **36** (2001) 1921–1929.
- 7) S. Ikeno, K. Matsuda, H. Matsui, T. Matsuki, T. Suzuki, N. Endou, T. Kawabata and Y. Uetani: *J. Mater. Sci.* (to be submitted).
- 8) I. Müllerová and L. Frank: *Scanning* **15** (1993) 193–201.
- 9) L. Frank and I. Mullerova: *J. Electron Microsc.* **48** (1999) 205–219.
- 10) I. Müllerová and L. Frank: *Adv. Imaging Electron Phys.* **128** (2003) 309–443.
- 11) K. Matsuda, S. Ikeno, I. Müllerová and L. Frank: *J. Electron Microsc.* **54** (2005) 109–117.
- 12) N. H. de Leeuw and S. C. Parker: *J. Am. Ceramics* **82** (1999) 3209–3216.
- 13) C. Wang and P. J. Zanzucchi: *J. Electr. Soc.* **118** (1971) 586–591.
- 14) X. Li, P. Pirouz and A. H. Heuer: *Phil. Mag. A* **65** (1992) 403–425.
- 15) X. Cao and J. Campbell: *Met. Mater. Trans. A* **34** (2003) 1409–1420.
- 16) R. C. Rossi and R. M. Fulrath: *J. Am. Ceram. Soc.* **46** (1963) 145–154.