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Microstructural development in Al/MgAl$_2$O$_4$ in situ metal matrix composite using value-added silica sources

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Abstract

Al/MgAl$_2$O$_4$ in situ metal matrix composites have been synthesized using value-added silica sources (microsilica and rice husk ash) containing ~97% SiO$_2$ in Al-5 wt.% Mg alloy. The thermodynamics and kinetics of MgAl$_2$O$_4$ formation are discussed in detail. The MgO and MgAl$_2$O$_4$ phases were found to dominate in microsilica (MS) and rice husk ash (RHA) value-added composites, respectively, during the initial stage of holding the composites at 750 °C. A transition phase between MgO and MgAl$_2$O$_4$ was detected by the scanning electron microscopy and energy-dispersive spectroscopy (SEM–EDS) analysis of the particles extracted from the composite using 25% NaOH solution. This confirms that MgO is gradually transformed to MgAl$_2$O$_4$ by the reaction

$$3\text{SiO}_2(s) + 2\text{MgO}(s) + 4\text{Al}(l) \rightarrow 2\text{MgAl}_2\text{O}_4(s) + 3\text{Si}(l).$$

The stoichiometry of MgAl$_2$O$_4$, $n$, computed by a new methodology is between 0.79 and 1.18. The reaction between the silica sources and the molten metal stopped after 55% of the silica source was consumed. A gradual increase in mean MgAl$_2$O$_4$ crystallite size, $D$, from 24 to 36 nm was observed in the samples held for 10 h.

Keywords: MgAl$_2$O$_4$, reactive wetting, stoichiometry, configurational entropy

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

MgAl$_2$O$_4$ (spinel) is one of the end members of the spinel group minerals, which have the general chemical composition of AB$_2$O$_4$, where A is a divalent atom such as Mg$^{2+}$, Fe$^{2+}$, Mn$^{2+}$ or Zn$^{2+}$ and B is a trivalent atom such as Fe$^{3+}$ or Al$^{3+}$ [1]. The anion is usually oxygen. The MgAl$_2$O$_4$ phase exhibits a congruent melting point at 2315 °C in the MgO–Al$_2$O$_3$ binary phase diagram [2]. MgAl$_2$O$_4$ exhibits a unique combination of properties such as a low thermal conductivity, a low coefficient of thermal expansion, good thermal shock resistance, a low dielectric constant and high electric resistivity [3]. Apart from being an important refractory material, it is used in advanced areas such as high-temperature arc-enclosing envelopes, humidity and infrared sensors, transparent windows, domes and armor materials [4]. MgAl$_2$O$_4$ can be considered as an important reinforcement in metal matrix composites (MMCs). In addition to its excellent combination of properties, metals (usually Al) adhere strongly without reaction to this oxide. Both MgAl$_2$O$_4$ and Al have a cubic structure, and the lattice parameter of the close-packed fcc oxygen anion sublattice of the MgAl$_2$O$_4$ unit cell
is nearly equal to that of the fcc aluminum unit cell, raising the possibility of forming low-energy interfaces between MgAl$_2$O$_4$ and aluminum for any orientation [5].

In practice, MgAl$_2$O$_4$ is produced by a two-stage firing process: calcining the powder mixture at 1600 °C to complete the spinelization reaction followed by ball milling or hot pressing, but usually the product contains a high percentage of nonstoichiometric spinel (MgO$_n$Al$_2$O$_3$), where $n$ is the stoichiometry of the spinel, which is equal to the ratio of Al$_2$O$_3$ to MgO) [6]. A few chemical techniques have been proposed for stoichiometric spinel fabrication [7–9]. However, in situ stoichiometric spinel in Al can be generated at a low temperature using silica sources [10–12]. Silica acts as an oxygen source for the fabrication of stable oxides such as MgAl$_2$O$_4$ or Al$_2$O$_3$ in Al–Mg alloy. The reduction of silica is thermodynamically and kinetically favorable, and the similar densities of amorphous silica and molten Al (2.3 g mL$^{-1}$) reduce the difficulties encountered during addition through the vortex method. Silica is also much cheaper than other oxygen sources such as CuO and ZnO. Furthermore, the availability of value-added silica sources such as microsilica and rice husk ash from industrial and agricultural waste, respectively, further reduces the cost of the process while reducing its environmental impact. Microsilica is the condensed form of submicron or nanosized silicon dioxide particles (mean particle size ~150 nm) and is obtained as a by-product from the production of silicon metal and ferrosilicon alloys [13]. Rice husk ash containing a high percentage of amorphous silica (>90%) is produced by burning rice husk under controlled conditions. Rice husk, an agricultural 'waste' material that is available in abundance in rice-producing countries, is also amenable for value-addition [14]. In this paper, we study the feasibility of forming MgAl$_2$O$_4$ in Al–5 wt.% Mg alloy using microsilica and rice husk ash as silica sources.

2. Experimental

Since characteristics such as the composition, surface area, microstructure and the amorphous nature of silica sources can affect the reaction kinetics, they were assessed by energy-dispersive spectroscopy (EDS), a nitrogen absorption technique (BET), scanning electron microscopy (SEM) and x-ray diffraction (XRD) analysis, respectively. 600 g of commercially available pure Al (Al 99.75 wt.%, Si < 0.1 wt.%) and 5 wt.% Mg as the starting materials were placed in a clay graphite crucible and melted in an electric resistance furnace. The addition of a 5 wt.% silica source was performed by the vortex method at a temperature between 730 and 750 °C. The melt was then held at 750 °C for 10 h and samples of 50 g each were taken from the furnace after stirring at 1 h intervals and allowed to solidify in a permanent mold. The microstructural analysis of the composite samples was carried out by both optical metallography and SEM. The chemical composition of the matrix alloy was determined by optical emission spectroscopy (OES) on particle-free areas. Partially reacted silica particles that were extracted from the composite samples using 25% NaOH solution were used for XRD and SEM–EDS identification of the possible phases, such as MgO and MgAl$_2$O$_4$, formed during the reaction between silica particles and the metal. Another set of samples containing only MgAl$_2$O$_4$, prepared using 35% dilute hydrochloric acid as an extraction medium since MgO is highly reactive with the acid, were used for measuring the stoichiometry, $n$, and the grain growth of the MgAl$_2$O$_4$ after different holding times through XRD analysis.

3. Results and discussion

3.1. Characteristics of silica sources

The compositions of microsilica and rice husk ash particles are given in table 1. The average particle surface areas of microsilica and rice husk ash were 17355 and 13502 m$^2$ kg$^{-1}$, respectively. Figure 1 reveals that the micro silica particles are spherical, whereas the rice husk ash particles shown in figure 2 have various shapes (spherical, platelets, etc.) containing a large number of open pores of micron size. Both the particles exhibit moisture-absorbing characteristics due to their porous nature. The amorphous nature of the silica particles was determined by the broadening of the peak observed at 2θ = 22.5° in the XRD pattern, which is attributed to the disordered cristobalite (figure 3). Figure 4 shows the size distributions of both particles. About 40–45 wt.% of microsilica and rice husk ash particles are in the size range of 180–250 and 250–355 μm, respectively.
3.2. Identification of phases

The reaction between the silica particles and the Al–Mg alloy was well evidenced by the microstructural studies of Al–5Mg–5microsilica and Al–5Mg–5rice husk ash composites, in which large amounts of Al–Mg–Si and Al–Si–Fe phases were detected (figures 5–7). The reaction products, MgO and MgAl$_2$O$_4$, were detected by XRD at $2\theta = 36.85^\circ$ and $42.7^\circ$ (figures 8 and 9) and as needles [15] and octahedral crystals, respectively, in SEM micrographs (figures 10(a) and (b)) of the extracted particles. A new phase was identified in the samples extracted using NaOH (figure 10) and its composition was determined by EDS as Al = 14.33, Mg = 27.41, O = 56.37 and Si = 1.9 (at. %). Furthermore, the Al/Mg ratio of the phase is 0.5, which is between those of MgO (Al/Mg = 0) and MgAl$_2$O$_4$ (Al/Mg = 2), and hence can be considered as an intermediate or a transition phase and closely related to MgO in composition. A distinct peak observed at $2\theta = 34.69^\circ$ (figures 8 and 9) is near to that of Al$_2$O$_3$ ($2\theta = 35.15^\circ$). However, this peak is found to disappear along with that of MgO in the XRD patterns of the particles extracted by HCl (figure 9). Moreover, the observed extra peak showed certain features of the intermediate phase in the present study. With this primary evidence, the peak observed at $2\theta = 34.69^\circ$ can be considered as that of a transition phase. The gradual transformation...
Figure 7. SEM micrograph of the matrix of Al–5Mg–5 microsilica composite after 10 h of holding at 750 °C.

Figure 8. XRD patterns of the partially reacted microsilica particles extracted from the composites after holding for different times.

Figure 9. XRD patterns of the partially reacted rice husk ash particles extracted from the composites after holding for different times.

Figure 10. SEM micrographs of microsilica particles extracted from Al–5Mg–5 microsilica composites after holding for (a) 0 h and (b) 10 h.

of MgO to MgAl$_2$O$_4$ with increasing holding time can be understood clearly from XRD and SEM analyses. The XRD patterns of microsilica-added samples exhibited a variation of the peak intensities of MgO, the transition phase and MgAl$_2$O$_4$ with respect to holding time (figure 8). The MgO and transition phase peaks are only present in the XRD pattern of the as-processed (0 h) sample. The MgAl$_2$O$_4$ peaks started to appear after 2 h of holding and the peak intensities increased with holding time. In contrast, the peak intensities of MgO decreased with increasing holding time. However, the peak intensity of the transition phase increased and then decreased with increasing holding time. After 10 h of holding, the major peaks were those of MgAl$_2$O$_4$ with a minor peak of the transitional phase in the XRD pattern of the extracted sample. Figure 11 shows the effect of the transition phase in the MgO–MgAl$_2$O$_4$ phase transformation, where the relative intensities of the latter phases (MgO and MgAl$_2$O$_4$) with respect to that of the former have been plotted. Similar to the earlier findings, the relative intensities of MgO and MgAl$_2$O$_4$ showed decreasing and increasing trends, respectively, with respect to holding time. Moreover, the relative intensity underwent a sudden decrease in the initial
stage of holding (0–4 h) for MgO and a sharp increase in the final stage of holding (7–10 h) for MgAl\(_2\)O\(_4\). However, during the intermediate stage of holding (4–7 h), both phases had low relative intensities while the transition phase was dominant. The coexistence of MgO and MgAl\(_2\)O\(_4\) with the transitional phase in a single particle during the transformation of MgO to MgAl\(_2\)O\(_4\) can be seen in figures 10(a) and (b). On the other hand, in the samples with added rice husk ash held for 0 and 10 h, MgAl\(_2\)O\(_4\) was found to be the major phase with minor peaks of both MgO and the transition phase in the XRD patterns (figure 9). However, the relative intensity of the transition phase with respect to that of MgAl\(_2\)O\(_4\) did not change appreciably with increasing holding time.

The important thermodynamically feasible displacement reactions possible during the reduction of SiO\(_2\) in Al–Mg alloy are given below [16].

\[
\text{SiO}_2(s) + 2\text{Mg}(l) \rightarrow 2\text{MgO}(s) + \text{Si}(l),
\]
\[\Delta G_{750°C}^o = -268.22 \text{kJ mol}^{-1}, \] (1)

\[
2\text{SiO}_2(s) + \text{Mg}_2\text{Si}(l) + 2\text{Al}(l) \rightarrow \text{Mg}_2\text{Al}_2\text{O}_4(s) + 2\text{Si}(l),
\]
\[\Delta G_{750°C}^o = -449.632 \text{kJ mol}^{-1}, \] (2)

\[
3\text{SiO}_2(s) + 4\text{Al}(l) \rightarrow 2\text{Al}_2\text{O}_3(s) + 3\text{Si}(l),
\]
\[\Delta G_{550°C}^o = -556.44 \text{kJ mol}^{-1}, \] (3)

\[
3\text{SiO}_2(s) + 2\text{MgO}(s) + 4\text{Al}(l) \rightarrow 2\text{Mg}_2\text{Al}_2\text{O}_4(s) + 3\text{Si}(l),
\]
\[\Delta G_{550°C}^o = -631.084 \text{kJ mol}^{-1}. \] (4)

It is well known that all dispersoids in suspension in the melt are surrounded by physically or chemically absorbed gas, as shown in figure 12, where particles are represented as spheres [17]. Ramani et al [18, 19] and Ramamohan et al [20] have explained the effect of the gas layer on the segregation and rejection of particles in Al/graphite composites prepared by the vortex method. To initiate the wetting of the particle surface, the molten metal has to overcome this gas layer. In the dynamic conditions of composite processing through the vortex method, the gas layer is ruptured by either the turbulence created in the melt or the reaction with the melt (the scavenging effect of Mg in Al alloy), causing the wetting of the surface of the particles with the molten metal. The surface inhomogeneities produce several reactive regions on the particle surface, where partially bonded atoms are available. The wetting associated with the reaction, or reactive wetting [21], starts at such regions and propagates by simultaneous reactions on the particle surface. At first, either reaction (1) or (2) takes place forming MgO or MgAl\(_2\)O\(_4\), respectively, at the interface between the particle and the molten metal. However, MgO forms more readily at the highly reactive regions due to the higher reactivity of Mg than Al and the preferential segregation of Mg atoms at the interface [22]. With increasing the holding time, the Al atom concentration increases at the interface and the MgO crystals start to react with Al and the unreacted SiO\(_2\) by reaction (4). This process undergoes different stages generating various transition phases and finally forms the stable MgAl\(_2\)O\(_4\) phase, as given below.

\[
\text{SiO}_2 + \text{MgO} + \text{A} \rightarrow \text{Transition phases containing Mg, Al, Si and O}
\]
\[
\begin{align*}
\text{Mg, Al, Si and O} & \quad \left(0 < \frac{\text{Al}}{\text{Mg}} < 2 \right) \\
+ \text{Si} & \rightarrow \text{MgAl}_2\text{O}_4 \quad \left(\frac{\text{Al}}{\text{Mg}} = 2 \right) + \text{Si}. 
\end{align*}
\] (5)

The transition phases, which are initially rich in Mgg, later become rich in Al. The low Si content (1.9 at.%) in the identified phase gives further evidence for the reaction (5). In addition, the higher concentration of Al atoms at the reaction sites enables the formation of MgAl\(_2\)O\(_4\). The coexistence of MgO and MgAl\(_2\)O\(_4\) crystals with the transition phase in microsilica and rice husk ash gives clear evidence for MgAl\(_2\)O\(_4\) formation by reaction (5). The Si atoms released by all the reactions start to diffuse into the molten metal and forms solid Mg\(_2\)Si using the Mg available in the matrix by the reaction

\[
\text{Si} + 2\text{Mg} \rightarrow \text{Mg}_2\text{Si}.
\] (6)

The reaction propagates into the interior of the particles simultaneously with the surface reaction. After the formation of the first layer of MgO or MgAl\(_2\)O\(_4\), Mg, Al and the released Si must diffuse through the reaction layer to undergo further development.
Figure 13. Si and Mg concentrations in the matrix alloy after different holding times of the composites.

reactions in the interior of the particles. The formation of MgAl2O4 and MgO from SiO2 is expected to result in 27 and 13.6% decreases in volume, respectively [23]. Owing to this contraction, there are expected to be gaps between the newly formed crystals or between the newly formed crystals and remaining SiO2. Liquid Al and Mg infiltrate into these gaps and form so-called ‘diffusion channels’, as suggested by Legoux et al [24]. The bulk reaction of the particles was found to cease with increasing holding time as the product crystals accumulated in the diffusion channels. This was studied by OES analysis of the matrix alloy held for different durations. The change in the Si and Mg contents of the alloy for different holding times is plotted in figure 13. The Si contents immediately after the addition of particles or at the beginning of holding (0h) were 0.65 and 0.85 wt.% for the composites with added microsilica and rice husk ash, which increased steadily and reached 1.2 and 1.28 wt.% after 10h of holding, respectively. On the other hand, the added silica source (5 wt.%) contributed 2.26 wt.% of Si to the Al–Mg matrix. Similarly, the Mg contents were 2.06 and 2.43 wt.% at the beginning of holding and 1.6 and 2.1 wt.% between 2 and 10h of holding in the microsilica and rice husk ash composites, respectively. Despite the formation of 5 wt.% Mg at the beginning of composite processing, the loss due to the oxidation and the consumption due to the reactions occurring during particle addition were appreciable. Interestingly, MgO and MgAl2O4 dominated the composites containing microsilica and in rice husk ash, respectively, at the beginning of the reaction.

3.3 Stability of MgAl2O4

The stability of MgAl2O4 at the holding temperature and Mg concentration was verified from various theoretical evidences such as the MgO–Al2O3 phase diagram [25], the stability diagram of the MgO/MgAl2O4/Al2O3 system [26] and the ternary phase diagram of Al–Mg–O [27]. The inversion nature of MgAl2O4 increases the configurational entropy of atoms upon their self-rearrangement to form stable crystals. This increases the solubility of Al and Mg atoms along with that of oxygen in MgAl2O4. However, the configurational entropy is negligible below 800°C and rapidly increases above 1000°C. For this reason, in the MgO–Al2O3 phase diagram, the solubility of MgO and Al2O3 in MgAl2O4 increases above 1000°C, whereas the ratio of MgO to Al2O3 is limited to 1:1 below 1000°C, resulting in the formation of stoichiometric spinel, i.e. MgAl2O4. The stability diagram of the MgO/MgAl2O4/Al2O3 system and the Al–Mg–O ternary phase diagram give a range of Mg concentrations in the matrix that stabilize the MgAl2O4 at a given temperature. The Mg range in the Al–Mg–O system required for the thermodynamic stability of MgAl2O4 is 0.11–10 wt.% at 1075°C and 0.7–1.2 wt.% at 723°C according to the ternary phase diagram and the stability diagram. The stability of MgAl2O4 has been studied in different MMCs [28–30]. MgO and MgAl2O4 were detected at the interface of 339Al2O3-silica-bound Kaowool (47%Al2O3/53%SiO2) composites in heat treatment studies by Smith et al [28] and the higher activation energy required for reaction (3) compared with the other reactions resulted in the absence of Al2O3. Lee et al [29] modeled the stability of MgO–MgAl2O4–Al2O3 for various Mg concentrations using oxidized SiC-reinforced Al–Mg alloys and found that MgAl2O4 is only stable when the alloy has 0.002–6 wt.% Mg content. Zhong et al [30] experimentally detected MgAl2O4–MgO crystals on an oxidized SiC surface in Al–Mg/SiC composite, where MgAl2O4 crystals were mainly found with 0.3 and 1 wt.% Mg, and a mixture of MgAl2O4 and MgO fine crystals with 5 wt.% Mg was formed as the reaction products.

3.4 Analysis of the stoichiometry (n)

Zawrah [31] employed a novel method of calculating the lattice constant, an, of nonstoichiometric spinel (MgO.nAl2O3). The same method was used with some modifications for the present study to calculate the stoichiometry of the spinel. As mentioned earlier, nonstoichiometric spinel is a solid solution of MgO and Al2O3. Furthermore, Al2O3 in its γ-Al2O3 form in the spinel phase (known as defective spinel, Al8/3V1/3O4) where V is a vacancy at an octahedral site) with a lattice constant of 0.729nm can dissolve in MgAl2O4 (stoichiometric spinel). In other words, nonstoichiometric spinel can be regarded as a solid solution of stoichiometric spinel and defective spinel. Therefore, one can write

\[
\text{MgO}_n \text{Al}_2\text{O}_3 \rightarrow \text{MgAl}_2\text{O}_4 + \frac{3}{4}(n - 1)\text{Al}_{8/3}\text{V}_{1/3}\text{O}_4. \tag{7}
\]

The lattice constant of MgO.nAl2O3, an, can be written as a weighted average value of those for MgAl2O4 and Al8/3V1/3O4; hence,

\[
a_n = \frac{a_0 + 3/4(n - 1)a_1}{1 + 3/4(n - 1)}. \tag{8}
\]

Rearranging the above equation gives the stoichiometry, n, of the spinel, i.e.

\[
n = \frac{4a_0 - 3a_1 - a_n}{3(a_n - a_1)}. \tag{9}
\]
are the standard lattice constant values of MgAl\textsubscript{2}O\textsubscript{4}. The values \(a\), stoichiometry, \(n\), and \(\theta\) are the Scherrer constant (0.905 nm) is lower then that of Mg\textsubscript{2}O\textsubscript{3} (0.085 nm), the mobility of Mg through MgAl\textsubscript{2}O\textsubscript{4} crystals is higher than that of Al. Moreover, Mg exhibits higher reactivity than Al, and elemental atoms of the former may be segregated at the interface. These factors can markedly change the stoichiometry of MgAl\textsubscript{2}O\textsubscript{4}.

### 3.5. Growth of MgAl\textsubscript{2}O\textsubscript{4} crystallites

To study the growth of MgAl\textsubscript{2}O\textsubscript{4} crystallites for different holding times, the mean crystallite size, \(D\), of MgAl\textsubscript{2}O\textsubscript{4} was determined from XRD broadening at \(2\theta = 36.85^\circ\) and evaluated using the Scherrer formula,

\[
D = \frac{k\lambda}{\beta \cos \theta},
\]

where \(k\) is the Scherrer constant (0.9 \times 57.3), \(\beta\) is the full width at half maximum (FWHM) intensity, \(\lambda\) is the wavelength of the x-ray radiation and \(\theta\) is the Bragg angle [35]. Figures 15 and 16 show the existence of a linear relationship between \(D\) and the holding time, with the former ranging between 24 and 36 nm. MgAl\textsubscript{2}O\textsubscript{4} crystals initially form on the interface between the silica particles and their growth depends on the diffusion of Al and Mg.
(from the matrix to the interface) and Si (from the SiO₂ lattice to the matrix). The large numbers of grown crystals restrict the interfacial diffusion of elements between the matrix and the silica particles, and hence diffusion through the crystals (lattice and grain boundary diffusion) starts to dominate. Even though the configuration entropy of MgAl₂O₄ is very low at 750°C, these results show that MgAl₂O₄ exhibits enhanced diffusion properties under the experimental conditions, resulting in the growth of larger crystallites.

4. Summary

(a) Al/MgAl₂O₄ in situ metal matrix composites have been synthesized using value-added silica sources (microsilica and rice husk ash) containing ~97% SiO₂ in Al–5Mg alloy.

(b) A new transition phase existing between MgO and MgAl₂O₄ has been identified and experimentally verified. This confirmed that MgO is gradually transformed to MgAl₂O₄ by a thermodynamically feasible reaction (equation (5)).

(c) MgO and MgAl₂O₄ were found to dominate in composites with added microsilica and rice husk ash, respectively, in the initial stage of holding the composites at 750°C.

(d) The reaction between the silica sources and the molten metal stopped after 55% of the silica source was consumed, and the mean MgAl₂O₄ crystallite size, D, increased gradually from 24 to 36 nm during holding for up to 10h.

(e) The stoichiometry, n, of the MgAl₂O₄ formed ranged between 0.79 and 1.18.

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