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Formation of spinel ($MgAl_2O_4$), MgO and pure Cu particles in Al–2Mg alloy–CuO particle composites

P. C. MAITY, P. N. CHAKRABORTY*
National Institute of Foundry and Forge Technology, Hatia, Ranchi 834 003 India
S. C. PANIGRAHI
Metallurgical Engineering Department, Indian Institute of Technology, Kharagpur 721 302, India

CuO particles were introduced into liquid Al–2Mg alloy by the vortex method to prepare an Al alloy–$MgAl_2O_4$ *in situ* particle composite, by reaction between CuO particles and the Al–2Mg alloy melt. Pure Cu, $MgAl_2O_4$ and MgO particles were detected in the particles extracted from the composites. DTA study showed partial dissolution of Cu in the matrix. Microhardness and hardness of the composites are higher than those of the base alloy. Both microhardness and hardness are higher for the Al–2Mg–2CuO composite than those of the Al–2Mg–5CuO composite. The hardness of the Al–2Mg–2CuO composite is remarkably high. The increase in microhardness has been attributed to the solid solution hardening effect with Cu as well as to the difference in CTE between the Al matrix and the particles. On the other hand, the improvement in hardness resulted from both solid solution hardening as well as the presence of hard particles such as $MgAl_2O_4$ and MgO.

1. Introduction

Aluminium matrix particle composites have attracted the attention of many researchers during the last decade due to their superior properties, such as specific modulus, tensile strength and wear resistance, compared to the conventional alloys [1–8]. Generally the reinforcing particles are directly incorporated into liquid Al to prepare the composites. However the problems encountered in this approach are the non-wettability of the particles by molten Al and excessive interfacial reactions that causes degradation of the mechanical properties [9]. It has been observed that the interface of the reinforcement and the matrix is susceptible to crack initiation and propagation during mechanical deformation. This may either result form non-wetting or be due to the extensive interaction between the reinforcement and matrix [4, 10, 11]. One approach to control the interfacial reaction is the variable codeposition of multiphase materials (VCM) process [9, 12, 13], where reinforcing particles are incorporated into a stream of atomized liquid metal. Liquid metal infiltration into fibre or particle preforms can also control the interfacial reaction [14], if the time for infiltration is minimized. Another approach to minimize the interfacial reaction is the preparation of *in situ* composites. In this method, the reinforcing phases are formed within the matrix by some chemical reaction between the matrix and some externally added compounds. The advantages expected in such composites are better compatibility of the phases formed *in situ* with the matrix, cleanliness of the interface and the possibility of producing the reinforcing phases with varied morphology [15]. Thus TiB_2 [16], TiC [17] and Al_2O_3 [18] particles have been formed in Al matrix by reaction between Al and some other externally added solid or gaseous elements/compounds.

The present work envisages the preparation of an Al–$MgAl_2O_4$ *in situ* particle composite by the addition of CuO particles into the Al melt. The free energy change for the reaction $2Al + 3CuO = Al_2O_3 + 3Cu$ is -1162.7 kJ at 700 °C. The negative sign of the free energy indicates that the above reaction will proceed with the formation of Al_2O_3 particles by oxidation of the molten Al. However when Mg is alloyed to Al, the oxidation of Al–Mg alloy can produce $MgAl_2O_4$ [19]. The Cu formed by the above reaction is expected to dissolve into molten Al. Hence to determine the feasibility of producing Al–$MgAl_2O_4$ *in situ* particle composites, both 2 and 5 wt % of CuO particles have been incorporated into Al–2Mg alloy. The products of reaction were identified by X-ray diffraction study (XRD) and electron probe microanalysis (EPMA). Differential thermal analysis (DTA) experiments were carried out in order to observe any further reaction during reheating of the composites and also to find any dissolution of Cu into the matrix. Mechanical properties of the composites

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* Retired.

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TABLE I Size analysis of CuO particles

Size range (μm)	> 88	87–49	48–20	19–5	4–1	< 1
wt %	4.38	23.25	40.20	29.78	2.38	0.00

were evaluated to determine the effect of *in situ* $MgAl_2O_4$ particle formation on the properties of the composites.

2. Experimental procedure

Commercially pure Al and Mg were used in the experiments. The size of the CuO particles (analar grade) was determined in a Malvern Instruments particle size analyser. The size analysis of the CuO particles is given in Table I. The composites were prepared by the vortex method. The required amount of CuO particles was slowly added into the vortex formed in molten Al–2Mg alloy at 700 °C by stirring it with a graphite impeller revolving at 1200 r.p.m. After the complete addition of the particles, the composite melt was solidified in a crucible in still air. Two composites were prepared with the addition of 2 and 5 wt % CuO particles, respectively. Specimens for DTA and EPMA were taken from the Al–2Mg–5CuO composite ingot solidified in the crucible. The DTA experiment was carried out in a Mettler 2000C analyser with α-Al_2O_3 used as a reference. The specimen for EPMA experiment was mechanically polished and etched with Keller's reagent. It was observed in a Jeol JCXA 733 analyser having an optical microscope attachment. For the X-ray diffraction study, part of both composite ingots was remelted at 700 °C and treated with 0.3 wt % heaxachloroethane (C_2Cl_6) to extract the particles. Single treatment with C_2Cl_6 could not separate the particles from the melt. After repeating the treatment two or three times, sufficient numbers of particles were extracted from the composites for the X-ray diffraction study. The X-ray diffraction experiments were carried out in a Siemens D 500 diffractometer using MoK_α radiation in the 2θ range 10 to 40 °.

For mechanical property evaluation, the composite ingots were remelted at 700 °C and were cast into 12 mm diameter × 120 mm long graphite moulds. Specimens were taken from the cast composites to measure microhardness and hardness. Microhardness of the composites was measured in a LECO Microhardness tester with 25 g load and hardness was measured in Vickers hardness tester with 1 kg load.

3. Results

3.1. DTA study

The DTA curves of the Al–2Mg alloy and Al–2Mg–5CuO composite are shown in Fig. 1a and b, respectively. In the curve for Al–2Mg alloy a small peak is observed at 603 °C. After returning to the base line, the broad peak due to the fusion of the matrix starts at 619 °C and is completed at 718 °C. The peak temperature (T_p) is 685 °C. In the composite with 5 wt % CuO dispersions, a minor inflexion is observed at 603 °C similar to the base alloy. However, the temperature corresponding to the deviation of the DTA curve from the base line (T_1) is found to be reduced for the Al–2Mg–5CuO composite. In the base alloy this temperature is 619 °C and for the composite it is 591 °C. The peak temperature is almost the same for the base alloy and the composite. But the slope of the curve from T_1 to T_p is different. The curve of this portion is steeper for the base alloy compared to the composite (Fig. 1). The lowering of T_1 and the changed form of the curve from T_1 to T_p are associated with the alloying of Cu and depletion of Mg from the Al matrix. As CuO reacts with molten Al–2Mg alloy, $MgAl_2O_4$, MgO and Cu forms in the composite as discussed later. Though pure Cu has been detected in the matrix, it is possible that some of the Cu reduced from CuO dissolves in the molten Al–2Mg alloy during the preparation of the composite. In Al–SiC composites, Si formed by the reaction between SiC particles and molten Al alloy is dissolved into the alloy [20, 21]. On the other hand, Mg must be depleted from the matrix with the formation of $MgAl_2O_4$ and MgO. Hence the lowering of T_1 and the change in the shape of the DTA curve from T_1 to T_p are associated with the redistribution of the alloying elements, such as Cu and Mg, in the molten alloy during the preparation of the composites.

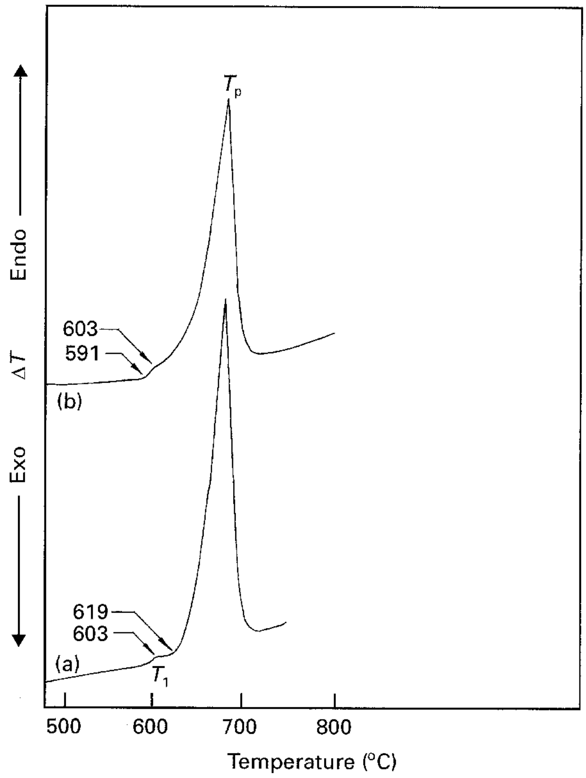

Figure 1 DTA curves of (a) Al–2Mg alloy and (b) Al–2Mg–5CuO composite.

3.2. XRD study and EPMA

To identify the phases/compounds formed in the composites, the particles were extracted from a portion of the composites by remelting and treating with

0.3 wt % heaxachloroethane (C_2Cl_6). Whereas a single treatment was sufficient to extract particles from Al–2TiO_2 composite [18], two or three treatments were necessary to extract the particles from Al–2Mg–CuO composites in the present work. The requirement for multiple treatments with C_2Cl_6 to extract the particles from Al–2Mg–CuO composites is due to the better wettability of the particles by Al–2Mg alloy as compared to pure Al. Mg is a reactive element and its addition to Al has been reported to improve the wettability of ceramic particles [22] by reducing the surface tension of the molten Al.

XRD study of the extracted particles from both Al–2Mg–2CuO and Al–2Mg–5CuO composites was carried out, whereas EPMA was done only for Al–2Mg–5CuO composite. The X-ray diffractograms of the particles from Al–2Mg–2CuO and Al–2Mg–5CuO composites are shown in Fig. 2b and c, respectively, in the 2θ range 15 to 40°. The X-ray diffractogram of CuO particles heat treated at 700 °C for 30 min is also shown in Fig. 2a; this acts as a reference for unreacted CuO particles which may be present in the extracted particles. The heat treatment of the CuO particles was intended to be similar to the conditions experienced by any unreacted CuO particles present in the matrix of the composites.

In the extracted particles from the Al–2Mg–2CuO composite, $MgAl_2O_4$, MgO, Cu and Al were detected. The presence of unreacted CuO in the composite was not confirmed as the strong peaks corresponding to CuO were close to those of $MgAl_2O_4$, MgO and Al. Al globules were observed visually in the extracted particles from both the composites. The pure Cu particles were found as red particles under the optical microscope. The $CuAl_2$ intermetallic phase was also detected by the X-ray diffraction study in the extracted particles. In the Al–2Mg–5CuO composite, similar phases were detected. The presence of unreacted CuO particles was not confirmed in this composite either.

The secondary electron image of the Al–2Mg–5CuO composite is shown in Fig. 3a and the WDS images of Cu, Mg, Al and O are shown in Fig. 3b to e. As pure Cu was detected by the WDS study, a red particle observed under the optical microscope attached to the EPMA was chosen for analysis. A Cu-rich phase is observed at the centre of the micrograph (Fig. 3a). Within this Cu-rich phase, the bottom part consists of both Al and Cu and the top is pure Cu. $CuAl_2$ was detected by the X-ray diffraction study. Hence the bottom part is probably $CuAl_2$ and the top part is pure Cu as shown in Fig. 3a. A sufficient amount of $MgAl_2O_4$ and MgO was detected in the composites by the X-ray study, but these phases

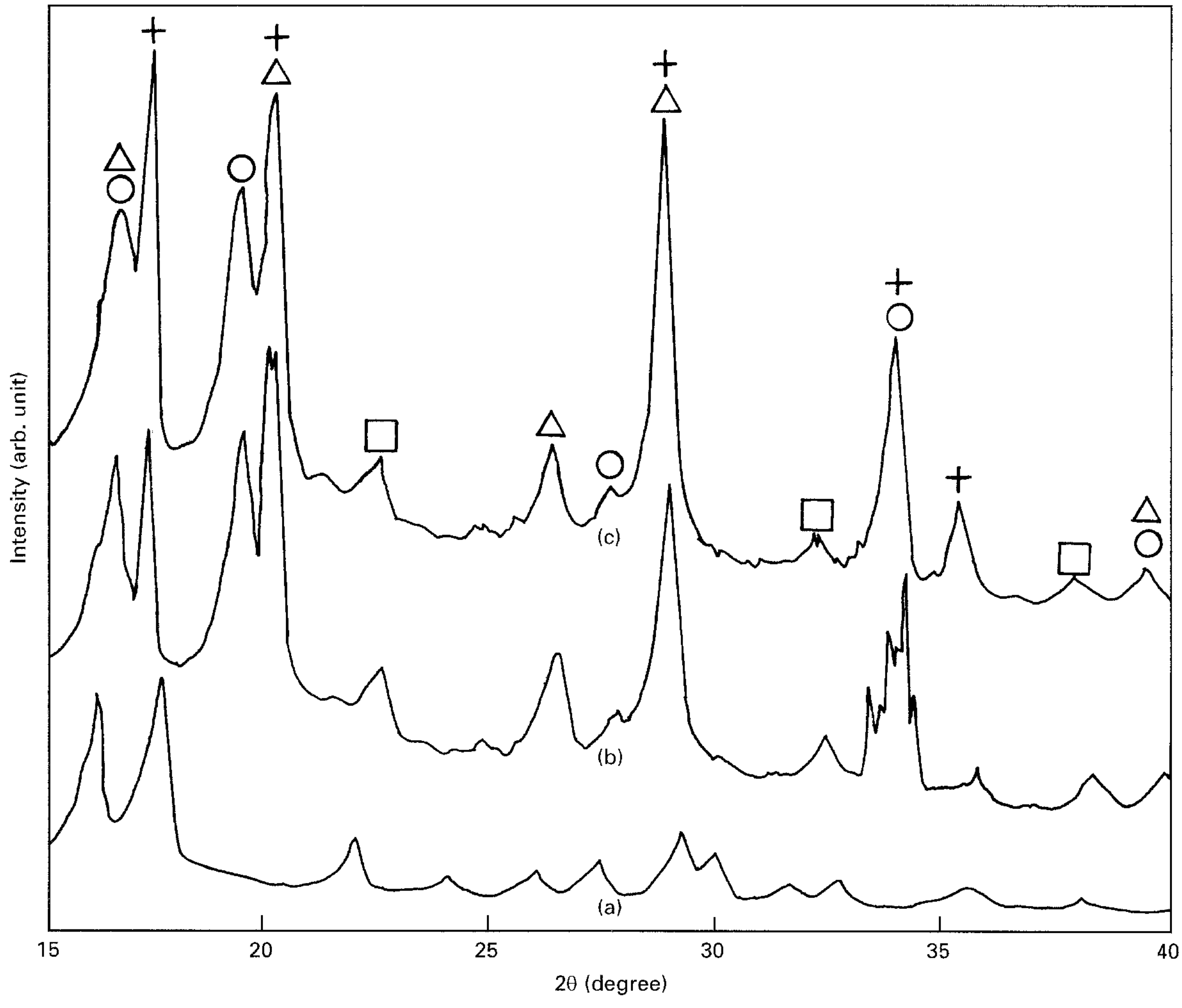

Figure 2 X-ray diffractograms of (a) heat-treated CuO particles, (b) extracted particles from Al–2Mg–2CuO composite and (c) extracted particles from Al–2Mg–5CuO composite. Key: △ $MgAl_2O_4$; □ Cu; ○ MgO; + Al.

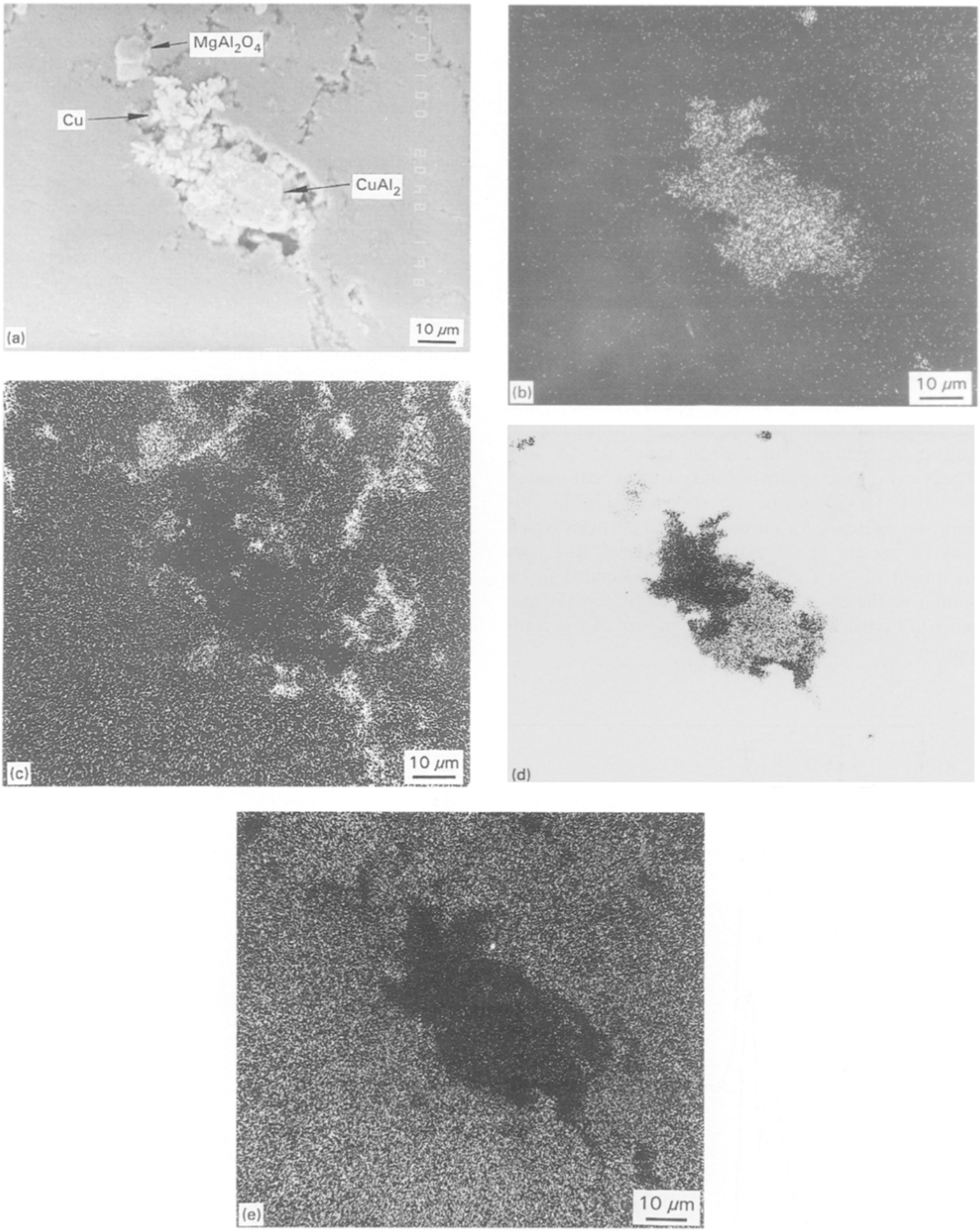

Figure 3 (a) Secondary electron image, (b) Cu X-ray image, (c) Mg X-ray image, (d) Al X-ray image and (e) O X-ray image of Al–2Mg–5CuO composite.

were not found in the neighbourhood of the Cu particle in a proportional amount. Only one small $MgAl_2O_4$ particle can be observed adjacent to the Cu particle. It indicates that the $MgAl_2O_4$ and MgO particles formed by the reaction between CuO particles and the molten Al–2Mg alloy are detached from the Cu particles and are dispersed into the matrix. Mg segregation is observed around particles in some locations.

3.3. Microhardness and hardness of the composites

The microhardness and hardness of the Al–2Mg alloy and the composites with the CuO addition are presented in Table II. Both the microhardness and hardness increased appreciably with the addition of CuO particles into Al–2Mg alloy matrix. It should be noted that the increase in both the microhardness and hardness is greater with 2 wt % CuO addition than with

TABLE II Microhardness and hardness of Al–2Mg alloy and Al–2Mg–CuO composites

Alloy/composite	Microhardness (VPN)	Hardness (VPN)
Al–2Mg	48.2	39.2
Al–2Mg–2CuO	79.0	103.3
Al–2Mg–5CuO	58.3	49.3

5 wt % CuO. For the base alloy the microhardness is greater than the hardness. On the other hand, the hardness of the Al–2Mg–2CuO composite is nearly three times that of the base alloy. In the case of the Al–2Mg–5CuO composite, the trend in the microhardness and hardness changes are same as those for the base alloy, i.e. microhardness is marginally more than the hardness value.

4. Discussion

The present work aims at formation of reinforcing particles such as $MgAl_2O_4$ in an Al matrix by the addition of CuO particles into an Al–2Mg alloy melt. Although work on CuO additions into an Al–Mg alloy has not previously been reported, the reactions of Al–Mg alloy with Al_2O_3 particles [23] and fibres [24–27] have been reported. Horng *et al.* [23] have studied the formation of $MgAl_2O_4$ in an Al–4Mg–Al_2O_3 particle composite. The particles were extracted from the composite by dissolving the matrix in aqua regia. The X-ray diffraction study of the extracted particles from the composite showed the presence of α-Al_2O_3 and $MgAl_2O_4$. The following reactions were proposed:

$$MgO(s) + Al_2O_3(s) = MgAl_2O_4(s) \quad (1)$$

$$3Mg(l) + 4Al_2O_3(s) = 3MgAl_2O_4(s) + 2Al(l) \quad (2)$$

$$Mg(l) + 2Al(l) + 2O_2(g) = MgAl_2O_4(s) \quad (3)$$

Levi *et al.* [24] have studied the interfacial reaction in an Al–Mg alloy with Al_2O_3 fibres [24]. The interaction zone consisted of $MgAl_2O_4$, MgO and fine polycrystalline α-Al_2O_3. It was suggested that the $MgAl_2O_4$ spinel formed by the reaction between Mg in solution and the Al_2O_3 fibres or fine α-Al_2O_3. The formation of α-Al_2O_3 was attributed to the oxidation of the Al melt. Similar reactions to Reactions 1, 2 and 3 have been proposed here. The presence of $MgAl_2O_4$ phase at the interface of FP-alumina fibres and Al–4Mg alloy matrix has been reported Munitz *et al.* [25]. Fishkis [26] has shown by an electron diffraction study that in Al–4.5Cu–3Mg alloy–saffil alumina composite, the interface consists of $MgAl_2O_4$, Al_2CuMg and $CuAl_2$. Molins *et al.* [27] have detected MgO, $MgAl_2O_4$, Mg_2Si and Si at the interface of Al–20 vol% saffil alumina fibres with 2 or 3% Mg. The reactions suggested are:

$$SiO_2(s) + \frac{4}{3}Al(l) = \frac{2}{3}Al_2O_3(s) + Si(s) \quad (4)$$

$$SiO_2(s) + 2Mg(l) = 2MgO(s) + Si(s) \quad (5)$$

$$2SiO_2(s) + 2Al(l) + Mg(l) = MgAl_2O_4(s) + 2Si(s) \quad (6)$$

The SiO_2 was used as the preform binder to prevent damage during squeeze casting.

The formation of $MgAl_2O_4$ and MgO is possible in an Al–4Mg alloy matrix containing oxidized SiC particles [20]. In oxidized SiC particles, SiO_2 forms on the surface. The following reactions were proposed:

$$2Al + Mg + 2SiO_2 = MgAl_2O_4 + 2Si \quad (7)$$

$$2Mg + SiO_2 = 2MgO + Si \quad (8)$$

In the present work, CuO addition into Al–2Mg alloy has formed $MgAl_2O_4$, MgO, Cu and $CuAl_2$ in the matrix of the alloy. CuO particles are highly reactive in the Al melt. The following reactions are possible:

$$Mg(l) + CuO(s) = MgO(s) + Cu(s) \quad (9)$$

$$2Al(l) + Mg(l) + 4CuO(s) = MgAl_2O_4(s) + 4Cu(s) \quad (10)$$

Pure Cu formed by the above reactions partially dissolves in the Al–2Mg alloy during the preparation of the composites. Some dissolution of Cu in the matrix was apparent from the DTA study and pure Cu particles were detected in the matrix by optical microscopy and EPMA. The increase in microhardness can be attributed to the dissolution of Cu in the matrix and the resultant solid solution hardening. On the other hand, Mg depletion from the matrix is obvious from Reactions 9 and 10. Hence the net alloying effect on the microhardness of the matrix is produced by the increase in percentage Cu and reduction in percentage Mg in the matrix. Since the microhardness of the composites is greater than that of the base alloy, it appears that the beneficial effect of dissolution of Cu which increases microhardness is greater than the matrix softening caused by the depletion of Mg. The improvement in microhardness of the composites is also possibly due to a difference in the coefficient of thermal expansion (CTE) between the particles and the matrix. The differential CTE produces a higher dislocation density in the matrix of Al–SiC [28] and Al–Al_2O_3 [29] particle composites. The CTE of $MgAl_2O_4$ is $9 \times 10^{-6}\,°C^{-1}$ and that of MgO is $14 \times 10^{-6}\,°C^{-1}$ [30] whereas for Al it is $23 \times 10^{-6}\,°C^{-1}$ [29]. Therefore, the microhardness of the composites could be improved by the higher dislocation density in the matrix generated due to the difference in CTE of the Al matrix and the $MgAl_2O_4$ and MgO particles.

Comparing the microhardness of Al–2Mg–2CuO and Al–2Mg–5CuO composites, the reduced microhardness of Al–2Mg–5CuO composite can be attributed to greater Mg depletion from the matrix. Because of the higher wt % of CuO particles in the Al–2Mg–5CuO composite, more Mg would be consumed from the matrix and hence greater Mg depletion is possible. Although the X-ray diffraction study showed a lesser extent of reaction in Al–2Mg–5CuO composite than the composite with 2 wt % CuO addition, still more Mg depletion is possible in the former due to its much higher particle content. The microhardness can also be reduced by the presence of porosity in the composite.

The hardness is remarkably improved for the Al–2Mg–2CuO composite (Table II) whereas it is less than this peak value for Al–2Mg–5CuO composite. The improvement in hardness can be attributed to both matrix hardening, as reflected in increased microhardness, as well as the composite hardening effect due to the presence of hard particles such as $MgAl_2O_4$ and MgO. The presence of reinforcing particles such as $MgAl_2O_4$ and MgO has been detected in both composites. Still the lowering of hardness with increased CuO addition is possible both due to lower microhardness and to the presence of more porosity in the structure seen for Al–2Mg–5CuO compared to Al–2Mg–2CuO. An increased level in porosity has been reported [31] with a higher wt % of particles in cast composites, especially when the preparation of the composite is associated with stirring of the melt. Optical microscopy showed a higher porosity level in the Al–2Mg–5CuO composite than the composite with 2 wt % CuO added. Therefore the greater Mg depletion and higher level of porosity reduces the hardness of Al–2Mg–5CuO composite to a minimum.

5. Conclusion

Up to 5 wt % of CuO particles could be incorporated into molten Al–2Mg alloy by the vortex method. $MgAl_2O_4$, MgO and pure Cu formed in both Al–2Mg–2CuO and Al–2Mg–5CuO composites as a result of the reaction between the alloy and the CuO particles. Part of the Cu formed by the reaction dissolved into the molten alloy during the preparation of the composites. The rest of the Cu remained in the matrix as pure Cu particles.

The microhardness and hardness of the composites are greater than those of the base alloy. The increase in microhardness is attributed to the dissolution of Cu in the matrix and the presence of a higher dislocation density in the matrix due to mismatch of the CTE of Al and $MgAl_2O_4$ and MgO. On the other hand, a decrease in microhardness is possibly due to the depletion of Mg from the matrix as well as to the presence of porosity in the structure. The hardness is improved by matrix hardening as well as by the presence of hard particles such as $MgAl_2O_4$ and MgO. The hardness of Al–2Mg–2CuO composite is remarkably improved. The microhardness and hardness of Al–2Mg–2CuO composite is higher than those of the Al–2Mg–5CuO composite. The reduced properties of the latter is attributed to more Mg depletion from the matrix and a higher level of porosity.

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