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On enhancing the interfacial chemistry of a simulated AA2014-SiC$_p$ composite material

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The use of aluminum alloys in automotive applications has increased significantly in recent years due to the need for more fuel-efficient vehicles. These alloys alone do not enjoy the strength offered by traditional ferrous products. However, the development of new alloys through micro/macroalloying and the incorporation of load-bearing materials such as SiC into the matrix have enhanced their popularity. Unfortunately metal matrix composites such as AA2014-SiC often fail catastrophically due to fibre or particulate pullout in service. Such failures are difficult to predict and are often a result of poor wetting at the metal/reinforcement interface. In the present work Sn and Ni were examined as potential sintering/wetting aids. In particular, Sn or Ni (0.5–2 w%) were added to a simulated AA2014 alloy (Al-4Cu-0.5Mg) with and without 14.5 w% SiC following standard powder metallurgy techniques. Because the distribution of blend constituents is of critical importance various dispersants were evaluated. Best particle dispersion was obtained using oleic acid while mixing for 8 h. Sintering temperatures ranged from 605–620°C and both green and final densities were determined using mercury densitometry. Resulting microstructures were examined using scanning electron microscopy and electron probe microanalysis with particular attention directed to the SiC-alloy interface. Nickel was found to enhance the wetting of SiC by AA2014 and the interfacial region was found to be chemically superior to a commercial copper-coated SiC product. Tin contributed to an increase in intermetallic formation. It is believed that the improved interfacial region was due to the presence of a small amount of liquid phase at the AA2014-SiC interface giving a chemical rather than the usual mechanical bond between reinforcement and alloy.

1. Introduction

Aluminum alloys have been used successfully in automotive applications due to desirable weight savings. However, such alloys have not always performed well in selected applications such as cyclic fatigue and high wear regimes; as well, corrosion resistance has been suspect. These concerns have led to the development of a variety of metal matrix composites (MMCs) using aluminum alloys as the matrix. MMCs offer several advantages over more conventional monolithic metal alloys. These include improved strength, stiffness, weight savings and fatigue resistance [1, 2]. Generally this is accomplished by combining a ductile metal matrix with a hard ceramic reinforcement such as alumina, carbon or SiC.

There are two main types of strengthening that may occur in a MMC; direct strengthening by transferring load from matrix to reinforcement and indirect, which involves a mechanical deformation of the matrix by the reinforcement and often occurs on heating [1]. With respect to fabrication of MMCs, the two most common methods are powder (P/M) and ingot (I/M) metallurgy. Each has its advantages but P/M tends to offer a better interface between matrix and reinforcement as well as the ability to produce complicated shapes with a minimum of machining steps [3].

One of the most popular MMC systems for automotive applications utilizes SiC particulates in an appropriate aluminum alloy. Such Al-SiC$_p$ composites require 10–20 vol% SiC and although they are attractive for reasons outlined earlier they also occasionally suffer from mechanical pull-out of the particulates while in service. Such an event is usually impossible to predict and thus may lead to catastrophic failure. As well, there is evidence that the environment may contribute to failure. For example enhanced wear rates have been experienced due to particle pull-out as a result of interactions between corrosion and erosion at the particle-matrix interface [4].

Because of the issues raised concerning particle pull-out it is evident that a large factor affecting the viability of a MMC is the metallurgical bond between matrix and reinforcement. With respect to Al-SiC it is well known that SiC is thermodynamically unstable when

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in contact with aluminum at moderate operating temperatures [5] and that an aluminum carbide will form unless Si is added to alter the thermodynamic equilibrium. However, unless there is some level of chemical interaction between phases the ultimate strength of the MMC will rely solely on the mechanical integrity of the interface. Of avenues available to enhance the interfacial region the addition of secondary elements, at either micro or macro levels, to the alloy to improve wetting is attractive. Various elemental additions have been investigated all with the intent of improving wetting of SiC in an aluminum matrix [6–8]. In particular, Sn has been reported to increase the densification and resultant tensile strength of an Al-Cu-Mg-Si alloy [9] and the wear resistance of a P/M AA2014 was also enhanced by microalloying with Sn [10]. Nickel has been reported to improve wettability in a similar fashion [11, 12]. Finally, a variety of particulate/fibre coatings is available to enhance wetting or reduce interfacial reaction. These include TiB_2 on carbon fibres for reinforcing Al and Cu, Ni, or Zn on SiC, again for Al-based MMCs.

With respect to corrosion, additions of Ag or Sn to AA2014 both resulted in a reduction in corrosion resistance [13] although Ag was found to out-perform Sn. This behaviour is believed to be due to the low solubility of Sn in Al causing the Sn to report to the grain boundaries. This in turn set up a small corrosion cell in the material leading to poor corrosion resistance. Conversely, Ag enjoys a uniform distribution throughout the sample and the potentiodynamic results reported reflect a material which has a noble metal addition [13].

Previous works by the authors have described a novel P/M approach to microalloying of aluminum alloys with Sn, Ca or Ag using a diffusion/supersolidus liquid phase sintering approach [14, 15]. The results underlined the important contribution of chemical composition and presence of intermetallics in the intergranular region to final mechanical properties. These findings together with earlier attempts to introduce natural minerals as strengthening agents in such alloys [16, 17] have prompted the present work that is focused on an examination of the influence of Sn or Ni on the interfacial chemistry of a P/M AA2014-SiC_p MMC. Included in the work are data relating final hardness and selected tensile values to sample microscopy and density as well as results from experiments to optimise blending times, dispersant type and sintering times. Because the intended application of the research is in the automotive field samples were not exposed to a post-sintering heat treatment/solutionising step. In such applications post-sinter densities in excess of 94% theoretical are deemed acceptable [18] and thus this was used as a guideline for the work.

2. Methodology

2.1. Materials

The matrix aluminum alloy used in the work was Al-4Cu-0.5Mg (w%). This was chosen to simulate AA2014, a popular alloy for automotive applications. The material was produced through inert gas atomization by Valimet, Stockton, CA, USA and was reported to be −200 mesh. The SiC (Norton product 7521, 600 grit, 99% purity) gave a d_{50} of 13.5 μm and the particulates were blocky in shape. Nickel (Inco T-123, 99.75% purity) had a d_{50} of 11.9 μm and the Sn (OMG Americas Reagent Grade) a d_{50} of 15.4 μm.

2.2. Sample preparation

2.2.1. Mixing

The powders were mixed in a 1L porcelain ball mill using 14 alumina cylinders as milling media. The SiC was dried overnight at 200°C in air; SiC (14 w% total mass) together with Al and Ni or Sn (0.5–2 w% total mass) as appropriate were blended. To reduce the tendency for agglomeration of the SiC and alloying additives during milling three dispersants were evaluated (50/50 oleic acid/benzene, 50/50 acetic acid/methanol, oleic acid; 0.2 ml per 100 gm powder). As well, three mixing times were examined (4, 8, and 16 h). Optimum conditions for the homogenous dispersion of Al + SiC were determined through visual examinations and were applied to all subsequent work.

2.2.2. Pressing/sintering

Mixed powders were hand packed into a 20 × 250 mm rubber mold, placed in a Loomis wet bag cold isostatic press (CIP) and pressed (187 MPa, 10 s). Samples were subsequently sectioned and sintered in a Lindberg SB tube furnace under a positive pressure of 99.99% argon. The thermal profile included a 10 min hold at 400°C to remove dispersant residue; sintering temperatures varied depending on blend composition (605–620°C). Three sintering times (1, 2, and 4 h) were evaluated using Al + SiC and the optimum used for all subsequent work.

2.3. Sample characterisation

2.3.1. Density

Both green and sintered densities were obtained using mercury densitometry techniques as an indication of the effectiveness of dispersant, blend time, sintering time and sintering temperature. Results were used to obtain an optimum P/M process to fabricate the samples and subsequently to evaluate the contribution of interfacial chemistry to the mechanical integrity of the Al-SiC_p MMC.

2.3.2. Microscopy

Extent of dispersion was visually qualified using optical as well as scanning electron microscopy (SEM-JSM 35). For the former, a standard mineralogical technique was employed whereby grains were sprinkled into a few drops of dispersant on a glass microscope slide and photographed whereas for the latter the substrate was a 1 cm diameter Al stub and the grains were dried and coated with Au. SEM as well as electron probe microanalysis (EPMA-JEOL 733 Superprobe) were used to assess the microstructure and complete quantitative chemical analyses for sintered specimens.

To reduce the accumulation of residual polishing debris in the pores of the sintered samples all were ultrasonically cleaned in methanol for 60s prior to examination.

2.3.3. Mechanical properties

Apparent hardness values were obtained to evaluate the influence of SiC, Ni and Sn on the Al matrix. Samples were ground through 600 grit SiC; a minimum of 5 measurements was taken for each. Although Rockwell B (1/16 in. steel ball, 100 kg) was used for most samples some with Sn addition were too soft. For these samples Rockwell E was used (1/8 in. steel ball, 100 kg) and the results compared using tabulated data [19].

Selected samples were subjected to tensile testing following ASTM E8M-99 [20]. Samples were machined to 6.35 mm gauge diameter, 36 mm length, 6.35 mm filets and were tested using an Instron test frame, maximum load 250 kN. Polycrystalline diamond tooling was used to machine samples containing SiC.

3. Results

3.1. Optimised sample preparation

A standard mixture of the Al-4Cu-0.5Mg (w%) ternary alloy and 14.5 w% SiC was used to evaluate sinter time/temperature, blend time and dispersant type. The 50/50 acetic acid and methanol mixture and a blend time of 16 h was used for the sinter time/temperature evaluation as this had been used in previous work on the system but without the presence of SiC [15]. All experiments are an average of replicate trials where values varied by ±0.1% in theoretical density. Three sinter times (1, 2, 4 h) and two temperatures (620, 630°C) were evaluated. Percent theoretical density values were obtained using mercury densitometry and compared to a theoretical density (2.9 g/cc) calculated for the ternary + SiC blend using the Rule of Mixtures. Best values were for a 4 h sinter at 620°C (93.3% theoretical). For comparison, values of 87–88% were obtained for the 1 h sinter and the value for 2 h at 630°C was 90.8%.

Blend times of 4, 8, and 16 h were examined using the standard mixture at 620°C for 4 h. A maximum % theoretical density of 94% was obtained for the 8 h blend time (vs. 93.6 and 93.3% for the 4 and 16 h blends respectively). Finally the three dispersants were examined using an 8 h blend and 4 h sinter at 620°C. The oleic acid proved superior (95% theoretical vs. 94.7 and 93.3% for the 50/50 benzene/oleic acid and 50/50 methanol/acetic acid respectively). Therefore, subsequent experiments used a blend time of 4 h with 0.2 ml of oleic acid and a sinter time of 4 h at 620°C (although the temperature was necessarily modified for mixtures containing Ni or Sn). A micrograph of the ternary + SiC using the standard conditions is given in Fig. 1 where the gray blocky grains are SiC.

3.2. Microscopy

3.2.1. Samples with nickel additions

Standard samples using the optimised process were examined with additions of 0.5, 1 and 2 w% elemental nickel to assess the effect of Ni in improving the wettability of Al/SiC. Elongated SiC-depleted zones were found on sintering at 620°C due to a high volume of liquid phase. Thus, temperatures of 615, 610 and 605°C were used for the 0.5, 1 and 2 w% Ni samples. Fig. 2 is a micrograph of the 2 wt% Ni sample showing distribution of the SiC and Ni whereas Fig. 3 and Table I are SEM and EPMA results for the same sample. With reference to Table I, point A represents the Al alloy, point B a SiC grain (theoretical Si in SiC is ∼70%), point C the wetting of SiC by Ni and point D the Ni alloyed with Al.

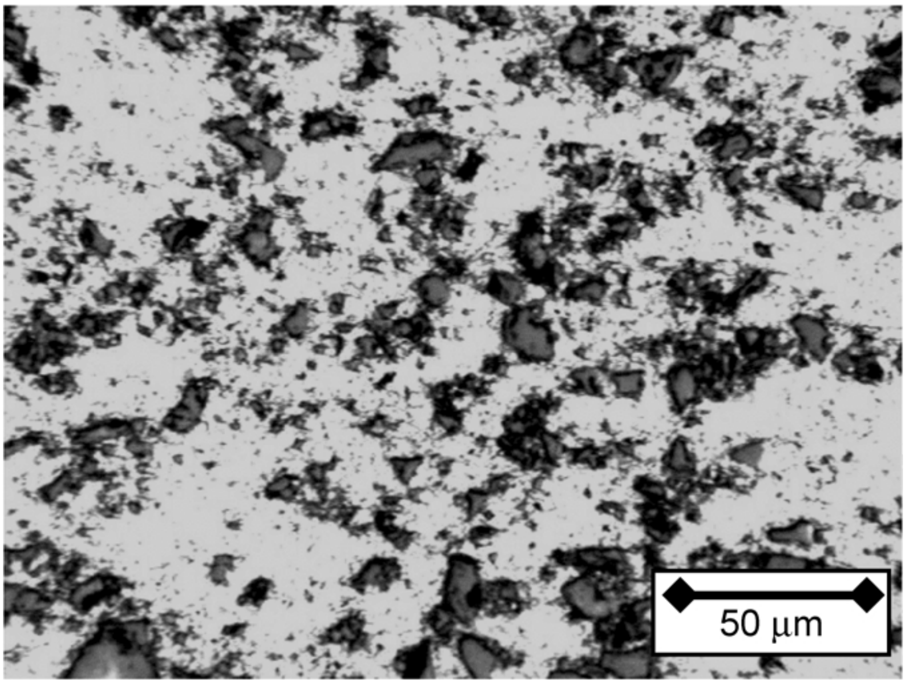

Figure 1 Optical micrograph of ternary alloy + 14 w% SiC, 8 h blend with oleic acid, 4 h at 620°C.

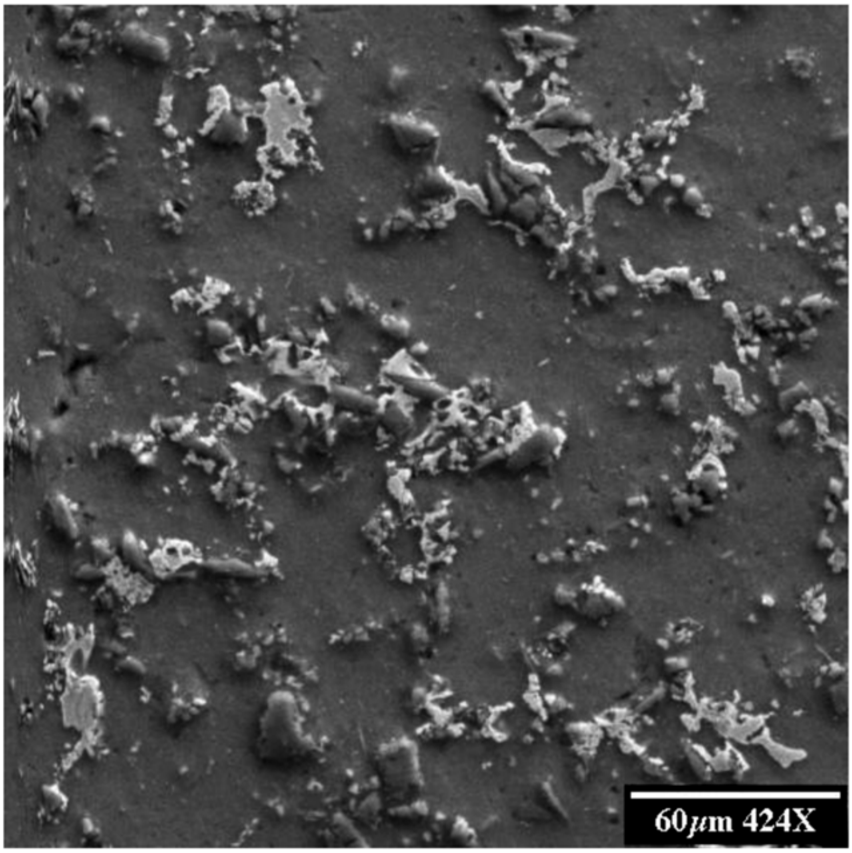

Figure 2 SEM micrograph of the ternary alloy + 14.5 w% SiC + 2 w% Ni.

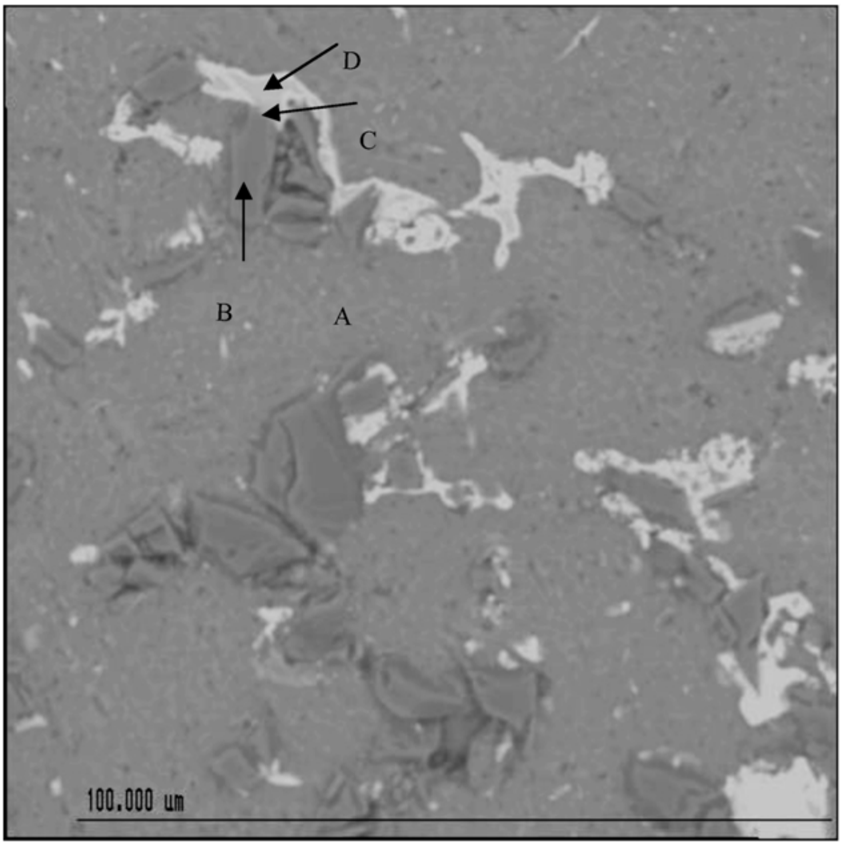

Figure 3 SEM micrograph of the sample in Fig. 2 showing grains for EPMA (Table I).

TABLE I EPMA analyses (w%) for selected grains in Fig. 3

Point	Al	Si	Cu	Ni
A	93.8	0.6	2.3	–
B	0.6	69.1	0.5	–
C	45.2	16.0	6.9	30.0
D	48.8	0.7	5.5	36.0

3.2.2. Samples with tin additions

Additions of 0.5–2 w% metallic tin were made to the standard blend. However, the 2 w% sample crumbled in the mould; changing the compaction pressure offered little improvement and thus experiments were confined to a maximum of 1 w% Sn. Representative micrographs for the ternary alloy, the alloy with 2 w% Sn and the 0.5 w% Sn sample (including X-ray maps for Cu and Si) are given in Figs 4–7 respectively. Of interest are the grain boundaries in Fig. 4, the location of Sn on the grain boundaries in Fig. 5 and the apparent volume fraction of particulates in Fig. 6a (well in excess of the 14.5 w% SiC added). As well, the location of Cu and Si in the X-ray maps of Fig. 6 and Si in Fig. 7 show the location of the SiC particulates relative to the presence of Sn. Finally, a commercial sample of SiC coated with Cu was examined for chemical integrity at the SiC/Cu interface. A representative micrograph is given in Fig. 8.

3.3. Mechanical properties

3.3.1. Hardness testing

Results for samples containing 0–1.5 w% Sn with and without 14.5 w% SiC are given in Fig. 9. Each set of values is based on a minimum of six indentations. For comparison wrought AA2014-O has a hardness of 87-98 HRH [21] (53-71 HRE). As might be expected, there is an appreciable decrease in apparent hardness as Sn is added. Although testing was also completed on specimens that contained varying levels of Ni, the resultant data were subject to wide scatter and were therefore deemed inconclusive.

3.3.2. Tensile testing

Selected samples containing Ni or Sn with and without SiC were prepared as outlined previously. Sn additions caused a notable decrease in the UTS of the base ternary alloy alone (Fig. 10) which correlates well with the noted effects of Sn on apparent hardness. Unfortunately, machining of the SiC-bearing samples proved difficult even when using polycrystalline diamond tooling and only a few values were obtained. In particular ultimate tensile strength (UTS) values of 182 and 193 MPa were

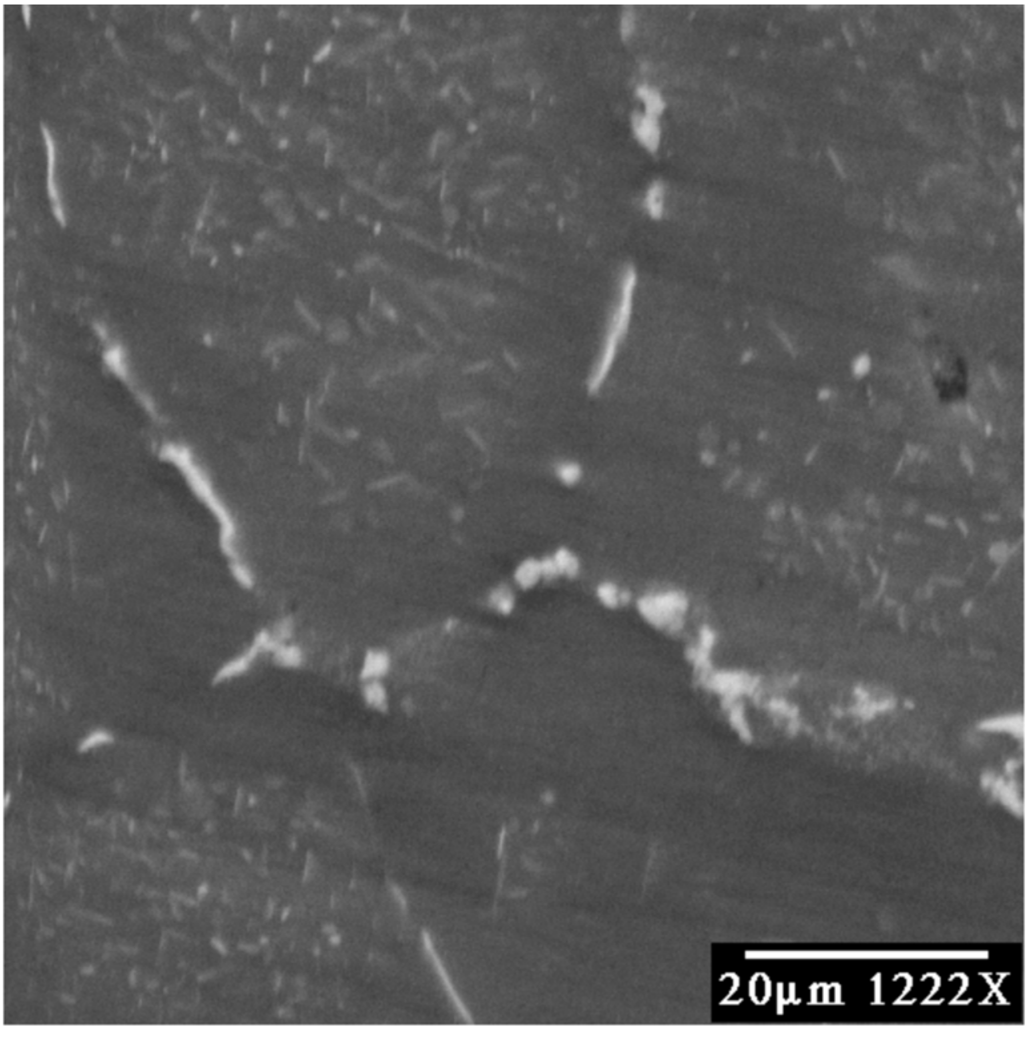

Figure 4 SEM micrograph of the base ternary alloy.

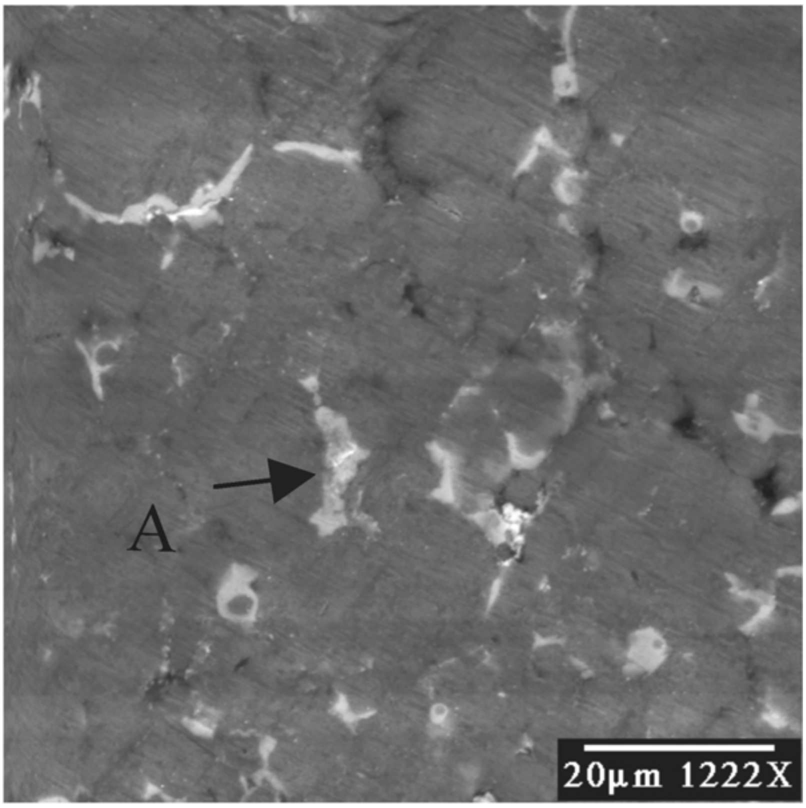

Figure 5 SEM micrograph of ternary alloy with 2 w% Sn. "A" represents Sn at a grain boundary.

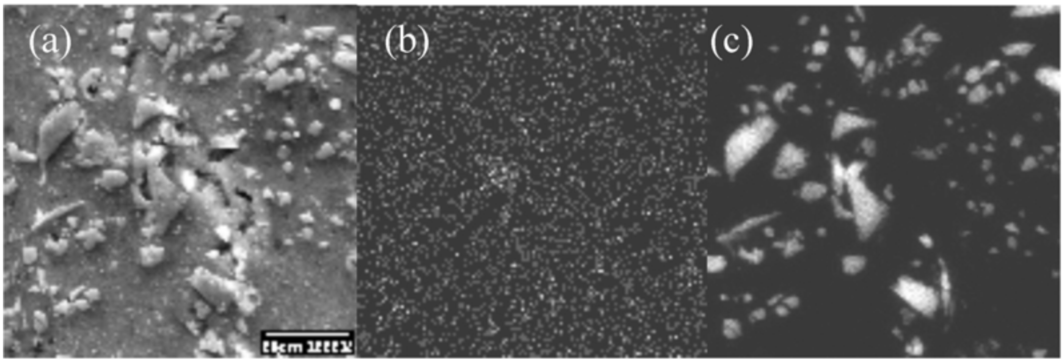

Figure 6 Micrograph of ternary alloy with SiC and 0.5 Sn. (a) SEM, (b) X-ray map for Cu, and (c) X-ray map for Si.

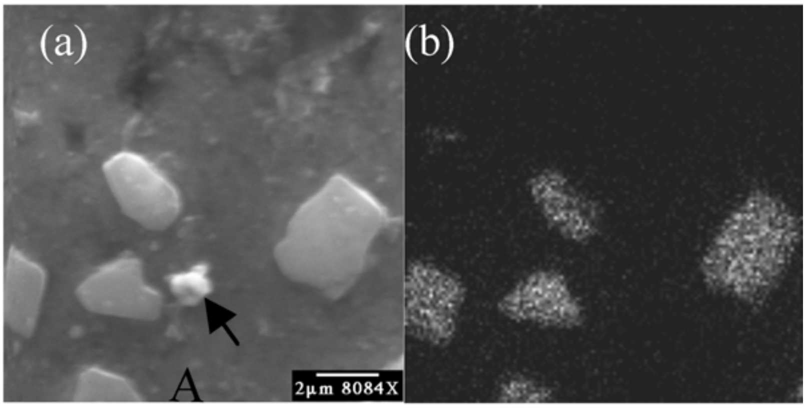

Figure 7 Higher magnification of Fig. 6. (a) SEM and (b) X-ray map for Si. "A" represents an aluminum copper precipitate.

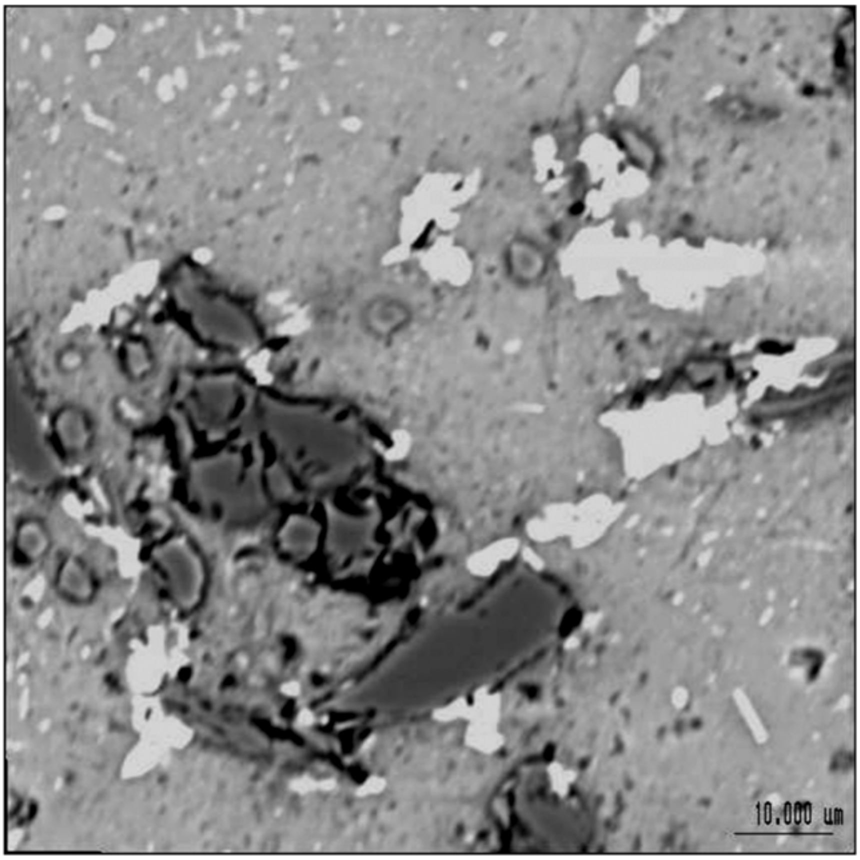

Figure 8 SEM micrograph of the ternary alloy with 14.5 w% Cu-coated SiC.

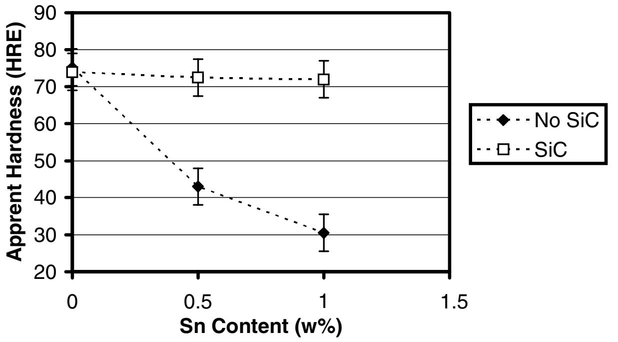

Figure 9 Plot of apparent hardness (HRE) as a function of SiC and Sn additions to the ternary alloy.

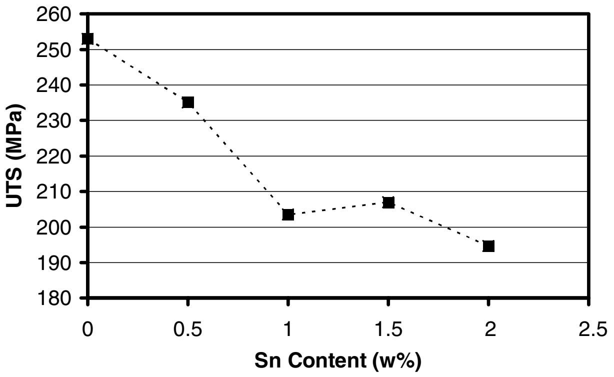

Figure 10 UTS as a function of Sn additions to the ternary alloy.

obtained for 1 and 0.5 w% Sn with SiC respectively whereas a sample with SiC only gave 190 MPa. The only value for Ni (0.5 w%Ni + SiC) was 153 MPa. This sample had a very low sintered density (86.2% theoretical) but still gave an elongation of 5.01% (vs. about 3% for the Sn + SiC samples).

4. Discussion

Examination of Fig. 1 confirms that the optimised conditions of 8 h blend time using oleic acid as dispersant followed by sintering at 620°C for 4 h provided a relatively homogeneous distribution of SiC for samples for the standard ternary alloy + SiC. Whereas previous work on the system utilized a post-sinter heat treatment followed by swaging to obtain near theoretical densities [14, 15] the present work was designed to follow industrial practice, both in terms of simplicity of sintering regime and associated acceptable theoretical densities (~94% [18]). As well, since the intent of the work was to investigate the interfacial region of an aluminum ternary alloy reinforced with SiC_p and the contribution of Ni or Sn as sintering aids, samples with densities in excess of 90% were considered.

With respect to nickel additions the micrograph in Fig. 2 suggests that the Ni (high reflectivity) has adhered to and thus coated the SiC particulates (low reflectivity). Equally important, the coated SiC grains are well distributed throughout the section; this is confirmation of the effectiveness of the dispersant/blending procedure. Fig. 3 and Table I provide further evidence that the Ni did indeed wet the SiC and therefore would be expected to provide enhanced density on sintering and, perhaps of greater importance, would help reduce particulate pullout and associated catastrophic failure of such parts in service.

The addition of Sn has been reported to increase both densification and tensile strength of a similar aluminum alloy [9]. Whereas it was possible to produce samples containing up to 1.5 w% Sn, samples with 2 w% were not mechanically sound after pressing in the CIP irrespective of pressure and time. Examination of Fig. 5 shows the Sn to be primarily at the grain boundaries in a fashion similar to the Al-Cu precipitates seen in the unmodified alloy (Fig. 4). Given the melting point of Sn relative to the sintering temperature (232 vs. 620°C) it is not surprising that this level of Sn addition would reduce mechanical integrity. However, for the ternary alloy with 0.5 w% Sn and the 14.5 w% SiC, it appears that on viewing Fig. 6a there has been a slight increase in the volume fraction of particulates in the sample. This may be a result of the Sn addition. The associated X-ray maps for Cu and Si (Fig. 6b and c respectively) show that the Cu is homogeneously distributed throughout the sample and the Si (SiC) grains are also well distributed. However, there are additional precipitates that are not SiC (Fig. 7) and, although too small for quantitative EPMA analysis given the resolution of the instrument, are thought to be Al-Cu intermetallics. Within the capability of the instrumentation it is suggested that an increase in Sn resulted in an increase in particulates. As well, small ($\sim 2\ \mu$m) grains of Sn (or an alloy of Sn) were found at the grain boundaries. Since the solubility of Sn in Al is very limited it appears that the Sn has enhanced the formation of particulates in the ternary aluminum matrix but has not taken part in the formation of a complex Sn intermetallic. Based on the findings an increase in toughness of the resulting MMC might be expected.

Interestingly, the micrograph shown in Fig. 8 of a commercial Cu-coated SiC sample shows that the Cu is present primarily as isolated metallic grains (high reflectively) rather than chemically bonded to the SiC. Whereas it is doubtful that Cu in this form would reduce SiC particulate pullout it is postulated that the process described in the present work for Ni should enhance performance of the MMC due to adherence of the Ni to the SiC.

An examination of the hardness data for Sn additions with and without SiC (Fig. 9) indicates a moderate decrease in hardness with Sn addition as might be expected. Sn is a relatively inert metal with respect to aluminum as it does not form any binary intermetallics nor does it exhibit any appreciable solid solubility. Consequently, Sn should be retained as discrete particles of soft, ductile material in the matrix. A decrease in both apparent hardness and UTS should result from its addition; reasoning that is directly supported by the data in Figs 9 and 10.

Finally, the tensile data given in Fig. 10 indicates that Sn additions gave a slight decrease in UTS. Compared to a nominal UTS of 219 MPa for AC2014-T1 [21] (the as-sintered value for the P/M equivalent of wrought AA2014), the PM ternary alloy containing Sn gave values ranging from 195–240 MPa. Furthermore, with additions of SiC UTS values were on the order of 180 MPa. Considering the difficulties encountered in machining the samples due to the presence of the SiC the results are encouraging.

5. Conclusions

1. An optimised procedure for preparing a powder metallurgy MMC using an alloy similar to AA2014 with 14.5 w% SiC has been developed. In particular, a blend time of 8 h using oleic acid as dispersant followed by sintering at 620°C for 4 h were found to be optimum.

2. The microstructure for samples containing additions of up to 2 w% Ni to the blend showed that the Ni adhered to the SiC particulates. Although hardness data for the samples were inconclusive there was evidence that the UTS was either improved or unaffected depending on level of Sn addition.

3. Comparing the potential benefit of Ni or Sn as a wetting agent/sintering agent for AA2014-SiC MMCs the microstructural study suggests that Ni would be more effective. Not only did the process followed provide Ni-coated SiC distributed homogeneously in the alloy matrix but the UTS values were encouraging in spite of the presence of up to 8% porosity and the difficulties associated with machining tensile specimens from aluminum MMCs containing SiC.

4. The final microstructure for the Ni samples appeared to be superior to that found for a commercial Cu-coated SiC product.

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