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Effects of copper addition on the sintering behavior and mechanical properties of powder processed Al/SiC$_p$ composites

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The effect of copper addition on powder processed Al-10 vol% SiC composites was studied in regards to their sintering responses. Copper was mixed with aluminum powder either as elemental powders or as the coated layer on SiC particles. After sintering at 600°C for 1 h, Al-SiC composites with no copper addition showed little densification. It also demonstrated very low bend strengths of 49 and 60 MPa, indicating poor bonding between the powders in the sintered composite. The addition of 8% copper to the Al/SiC system effectively improved the sintering response, producing over 95% theoretical density, a bend strength of 231 MPa with the copper coated SiC, and a 90% density with over 200 MPa bend strength with the admixed copper.

The as-sintered microstructures of the Al–SiC composites clearly revealed particle boundaries and sharp pores, indicating that only a limited neck growth occurred during sintering. In the case of Al–Cu–SiC composites, however, a liquid phase was formed and spread through particle boundaries filling the interfaces or voids between SiC particles and the matrix powders. The coated copper on SiC particles produced a somewhat better filling of the interface or voids, resulting in a little more densification and better sintered strength. Since the solubility of copper in aluminum is less than 2% at the sintering temperature, the alloying of copper in the aluminum matrix was limited. Most of the copper added was dissolved in the liquid phase during the sintering and precipitated as $CuAl_2$ phase upon cooling.

1. Introduction

Aluminum base composites, particularly Al/SiC composites have attracted great attention in recent years to modify or to improve properties, such as stiffness, strength, wear resistance and thermal expansion characteristics of monolithic aluminum alloys [1–3]. Continuous fiber reinforced composites can yield well tailored properties; however, their usage has been limited to mostly expensive components such as aerospace structures because of a high manufacturing cost [4]. Particulate reinforced composites can be produced at a relatively low cost by casting or the powder process. However, this results in some reduction of properties. In casting, SiC particles are dispersed in the liquid aluminum but their low wettability to liquid aluminum often causes the agglomeration of the particles. This can result in non-uniform properties and premature failures [5]. In addition, the reaction between the molten aluminum and SiC forms a brittle Al_4C_3 phase at the Al/SiC phase boundary and results in detrimental effects on the mechanical properties [5–7]. On the other hand, the conventional powder metallurgy process (PM) can easily formulate different compositions by simply mixing elemental powders and consolidate and sinter the powder mixtures to near net shape [2, 5]. However, most of the PM Al/SiC composites are fabricated by a hot consolidation process such as hot pressing or extrusion to simple shapes rather than utilizing the low cost press and sinter technique. This is due to the fact that the composite powder mixtures are more difficult to compact and sinter than monolithic aluminum powder mixtures and the resulting properties are generally not satisfactory [4, 8].

In a metal matrix composite (MMC), cohesiveness between the matrix and the reinforcing particles is also an important factor affecting the mechanical properties of the MMC. Stronger interfacial adhesion can distribute an applied stress more effectively to both the matrix and reinforcing particles, thus increasing elastic modulus, strength and wear resistance. Such interfacial

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cohesiveness is considered to depend on many factors such as interfacial energy between the matrix and the particles or the wetting of solid particles by a liquid phase [5, 7, 9, 10]. Previous research has demonstrated that the improved wetting of SiC particles by molten aluminum during the casting of Al/SiC composite through the utilization of SiC particles coated with nickel or copper increased the tensile strength and stiffness of the composite [6, 11, 12]. This indicates that the sintered properties of the Al/SiC powder composite can be raised by improving the bonding between matrix powders and the cohesiveness of the SiC particles to the matrix during sintering.

Liquid phase sintering is often employed in various powder alloy systems to increase the sintering rate. When the liquid phase persists during sintering, it can pull and braze the powders together by a capillary force. It also acts as a quick diffusion channel between the powders throughout the sintering cycle, thus increasing the sintered density and bonding [13]. However, when the liquid phase is transient, the liquid phase formed is dissolved in the solid matrix during the sintering process. This often causes swelling, as well as the formation of coarse and connected pores in the sintered structure [14]. Since the transient liquid exists only temporarily during the sintering cycle, its effect on enhancing the sintering is also limited. Aluminum powder can be mixed with many different elemental powders such as Cu, Mg, Zn, etc. to form liquid phases during sintering. Different alloying elements should produce liquid phases of different characters and exert different effects on the sintering. In order to assess the effects of these elements on an individual basis and select the best element for incorporating SiC particles, a preliminary sintering experiment was conducted for binary powder mixtures of aluminum powder with Cu, Mg and Zn powders. The results illustrate that 4–10% copper can form a persistent liquid phase by alloying with aluminum. On the other hand, Mg or Zn formed a transient liquid phase which was dissolved almost completely in the solid aluminum matrix during sintering, leaving many coarse pores in the sintered structures.

A persistent liquid phase is expected to be more effective than a transient liquid phase for improving the sintering of the composite powder containing SiC particles because it can penetrate the boundaries and glue the particles to the aluminum matrix instead of disappearing into the matrix. Also the copper alloying can raise the strength of the composite product by age-hardening. Based on these reasons, we selected copper powder as the alloying element to Al and SiC powder mixture. Two methods were employed for the copper addition: The first is a simple mixture of elemental copper powder with aluminum and SiC particles. The other is a mixture of aluminum powder with copper coated SiC particles which contain about 40% of copper by weight in the form of the coated layer. The latter was employed to see if any further improvements of the cohesiveness between the matrix and the SiC particles could be made. In order to match the copper content in both methods and to form a sufficient amount of the liquid phase to fill the boundaries and the pores, the copper content in the composites were fixed at 7.3% by weight.

2. Experimental procedure

2.1. Raw powders

A commercial air-atomized aluminum powder of −200 mesh (<75 μm) and electrolytic copper powder of −325 mesh (<45 μm) were used as the matrix powders. As the reinforcing phase, either pure SiC particles of 8 and 44 μm or copper-coated SiC particles of 44 μm (average size) were utilized. The copper-coated SiC particles contain 40 wt% of copper when analyzed by inductively coupled plasma (ICP). Fig. 1 shows SEM micrographs of the smooth and irregularly shaped aluminum powder and the angular shaped SiC particles. The coated SiC particles are covered with continuous copper layers of 1–2 μm thickness.

2.2. Compaction and sintering

The raw powders were mixed in a V-type mixer for 30 min at 55 rpm for each of the three compositions listed in Table I. All the blends were designed to contain 10 vol% of SiC. Compaction was done at room temperature in a double action die using Kenolube^{TM} as the die wall lubricant. Rectangular specimens of 31.7 × 12.7 × 6.35 mm for the three point bending test (ASTM B312-96 specification) and 58 × 13 × 13 mm for the tensile test (ASTM E8 specification) were compacted to 85 ± 1.5% theoretical density. The compacts were delubricated at 400°C for 30 min, sintered at 600°C for 1 h in a $3N_2 + H_2$ mixed gas atmosphere and then furnace cooled. All the sintered specimens were measured for dimensional change and density.

2.3. Mechanical properties evaluation

Three point bending tests were conducted on the sintered specimens in accordance with ASTM B312-96 specification, at the cross head speed of 2.5 mm/min using an Instron^{TM} testing machine. Tensile testing was conducted per ASTM E8 specification at 0.5 mm/min cross head speed for subsize round specimens of 20 mm gage length and 5 mm diameter machined from the sintered bars. Three specimens were tested for each batch using a pair of threaded grip and the results were averaged. For selected specimens, the microstructure and fractured surface were examined using SEM.

TABLE I Composition of powder mixtures

Specimens	Al	Cu (wt%)	SiC (wt%)	Theoretical density (g/cm^3)
Al–SiC	Bal.	0	11.54	2.75
Al–Cu–SiC	Bal.	7.3	10.95	2.89
Al–Cu coated SiC	Bal.	7.3	10.95	2.89

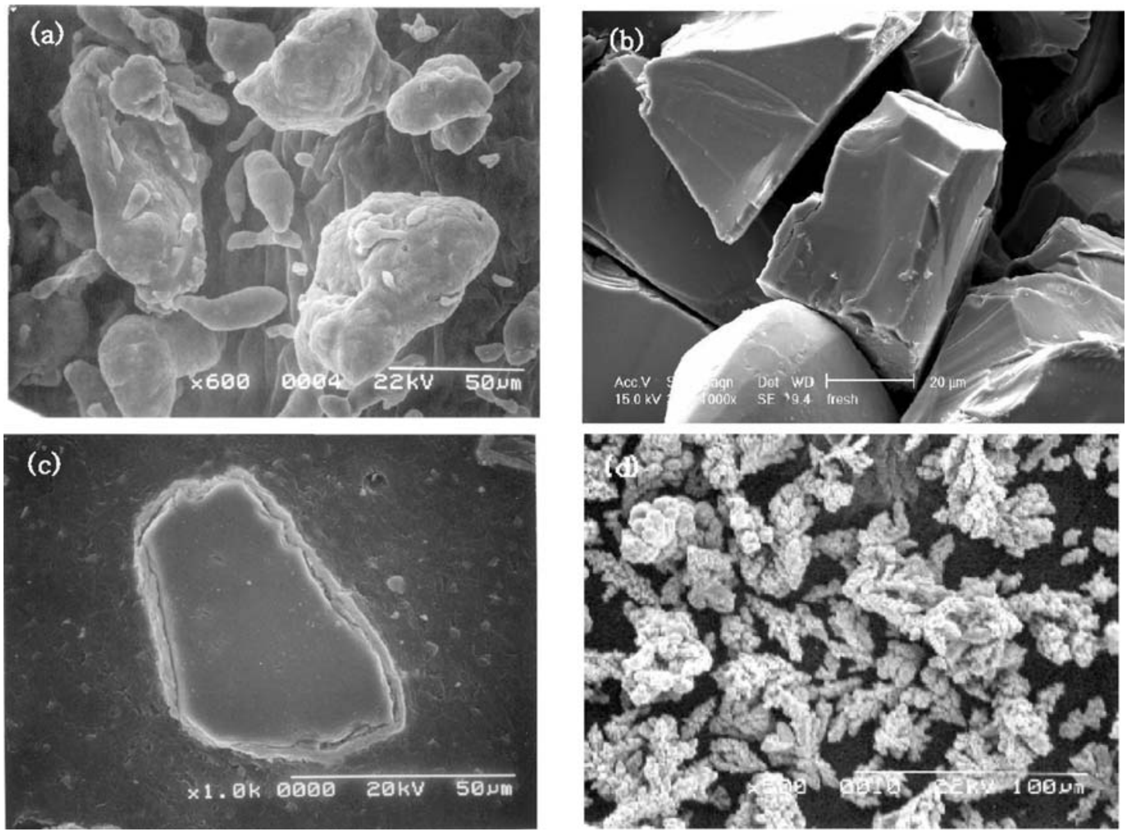

Figure 1 Scanning electron micrographs of raw powders: (a) Aluminum, (b) 44 μm SiC, (c) Cross-section of Cu coated 44 μm SiC, and (d) electrolytic copper.

3. Results and discussion

3.1. Sintering behavior

Density or dimensional change after sintering reflects the progress of the sintering. The average sintered densities of the three specimens for the 5 experimental blends which were compacted to 85% theoretical density are shown in Table II. The Al–SiC compacts showed less than 1% of density increase after sintering. On the other hand, the Al–Cu–SiC compacts were densified to over 90% theoretical density by the sintering at 600°C. Table II also shows that the compacts containing 44 μm SiC particles densified more than those containing the finer 8 μm particles, and the coated copper on SiC particles produced more densification than the admixed copper. The sintered microstructures in Fig. 2 clearly show the effects of copper addition on the sintering of the compacts. In the sintered Al–SiC composites of both Fig. 2a and b poor inter-particle boundaries, many sharp pores at particle junctions, and voids between the SiC particles are clearly visible. By comparison, the sintered composites alloyed with copper show much denser structure, containing a second phase which apparently is a solidified liquid phase. The liquid phase filled most of the inter-particle boundaries, pores and also some portion of the voids associated with the SiC particles. This indicates good wetting of the liquid phase to the aluminum matrix powders (Fig. 2c–e). The much higher sintered densities of the Al–Cu–SiC compacts after sintering can be attributed to the persistent liquid phase formed by the alloying between the elemental aluminum and copper powders during sintering. The void filling around the SiC particles appears more effective when the copper was alloyed by the coating. More voids were found to be associated with 8 μm SiC particles than with 44 μm SiC particles, and the finer particles have more tendency to agglomerate than the coarser ones. The voids between these agglomerated hard particles are difficult to fill by the matrix powders during compaction and remain as voids after sintering (see Fig. 2a–d). The XRD pattern (Fig. 3) reveals that the sintered composite contains only α-aluminum and $CuAl_2(\theta)$ phase without showing any copper or other intermetallic compounds, indicating that copper was completely dissolved during the sintering. EDS point analyses indicates that the α-aluminum matrix (A in Fig. 2) contains only 1–2% copper while the solidified phase (B and C in Fig. 2) contains 30–40% copper (Table III). This shows that most of the copper was dissolved in the liquid phase and precipitated as $CuAl_2(\theta)$ phase upon cooling and only a small portion of copper was alloyed in the matrix.

TABLE II Density of sintered composites at 600°C under $3N_2 + H_2$ for 1 h

Composites	Sintered density (%)
Al–8 μm SiC	85
Al–44 μm SiC	86.2
Al–Cu–8 μm SiC	90
Al–Cu–44 μm SiC	93
Al–Cu coated 44 μm SiC	96

Based on the above results and Al-Cu phase diagram in Fig. 4, the sintering of mixed elemental Al–Cu–SiC compacts can be described as follows: A limited

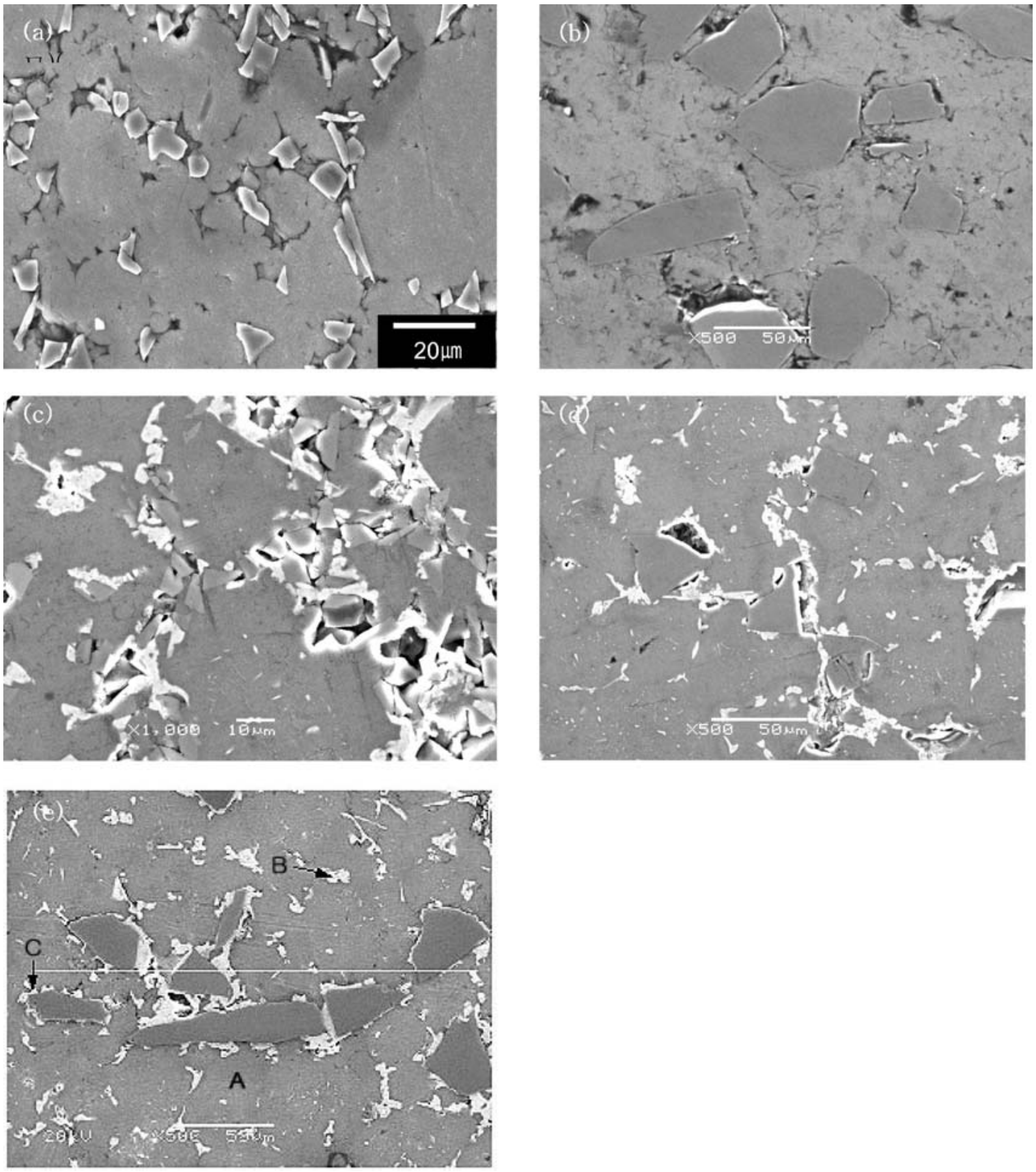

Figure 2 SEM micrographs of experimental specimens sintered at 600°C for 1 h: (a) Al-8 μm SiC, (b) Al–44 μm SiC, (c) Al–Cu–8 μm SiC, (d) Al–Cu–44 μm SiC, and (e) Al–Cu coated 44 μm SiC.

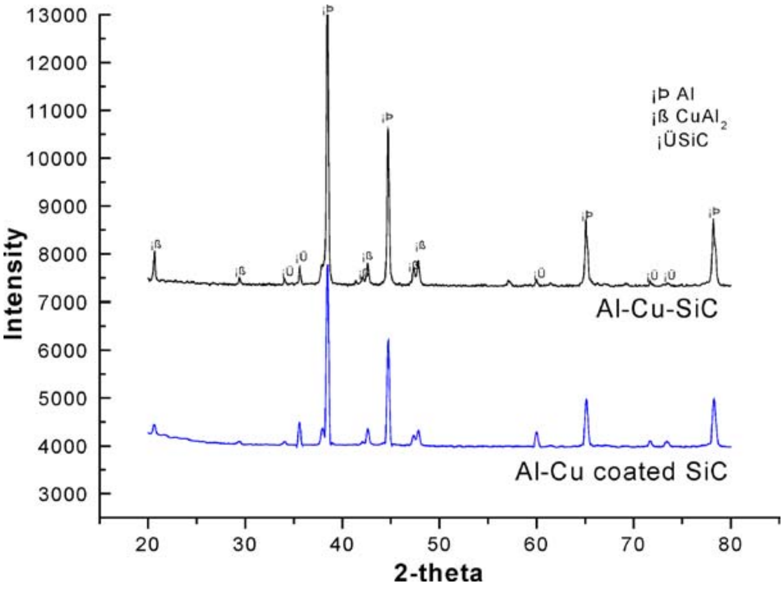

Figure 3 X-ray diffraction patterns of Al–Cu-44 μm SiC and Al–Cu coated 44 μm SiC after sintering at 600°C for 1 h.

TABLE III EDS analyses of matrix (A) and solidified phases (B and C) in Fig. 2e

	Al (wt%)	Cu (wt%)
A	95.84	1.04
B	59.2	32.48
C	62.54	37.24

alloying by solid state diffusion occurs at the contacts between the aluminum and copper powders during the holding period for delubrication and heating to the eutectic temperature of 548°C where the solubility of copper in aluminum is the maximum of 5.68 wt%. Further heating to the sintering temperature decreases the solubility of copper to less than 2 wt%, leading to the formation of a liquid phase in the surface region of aluminum powders containing more than 2 wt% copper. Since the liquid phase has a much greater solubility of copper, e.g., >50 wt%, at 600°C, it dissolves more copper and becomes enriched with copper within the range between b and c in Fig. 4. Once the liquid phase is formed, it spreads through the boundaries between the powders by a capillary force and fills pores and voids. Because of the limited solubility of copper in the solid aluminum matrix at the sintering temperature, the alloying of copper in the aluminum matrix should be limited to less than 2 wt%. When the sintered compact is cooled to room temperature, the liquid phase transforms to α-aluminum and $CuAl_2(\theta)$ phase. The relative portion of each phase in the solidified phase is governed by the copper content in the liquid phase, that is, a higher copper content produces more $CuAl_2(\theta)$ phase. Any copper-rich intermetallics which might have formed during the early stage of sintering must be dissolved in the liquid phase as well.

TABLE IV Transverse rupture and tensile strengths of sintered composites at 600°C for 1 h

Composites	TRS (MPa)	Tensile strength (MPa)
Al-8 μm SiC	49	–
Al-44 μm SiC	60	–
Al–Cu-8 μm SiC	206	104
Al–Cu-44 μm SiC	220	122
Al–Cu coated 44 μm SiC	231	128

When copper is alloyed by the coated layer around SiC particles, the liquid phase should initially form around the SiC particles and fill the adjacent voids first before spreading through the matrix. However, when copper is mixed as elemental powders, the liquid phase should form at the contacts between the aluminum and copper powders and fill the boundaries and pores first, leaving more unfilled voids around SiC particles. Therefore, the former can yield better sintering, particularly around the SiC particles than the latter, as is evident by the higher sintered density.

3.2. Mechanical properties

Transverse rupture strengths (TRS) and tensile strengths (TS) of the sintered Al–SiC and Al–Cu–SiC composites are presented in Table IV. The Al–SiC composites yielded very low TRS of 49 and 60 MPa with 8 and 44 μm SiC particles, respectively, whereas mixed elemental Al–Cu–SiC composites exhibited TRS values of over 200 MPa. A slightly higher strength of 231 MPa was obtained with the copper-coated SiC particles than with the mixed elemental Al–Cu–SiC composites which yielded 206 and 220 MPa with 8 and 44 μm SiC particles, respectively. The TS of mixed elemental Al–Cu–SiC composites also show similar

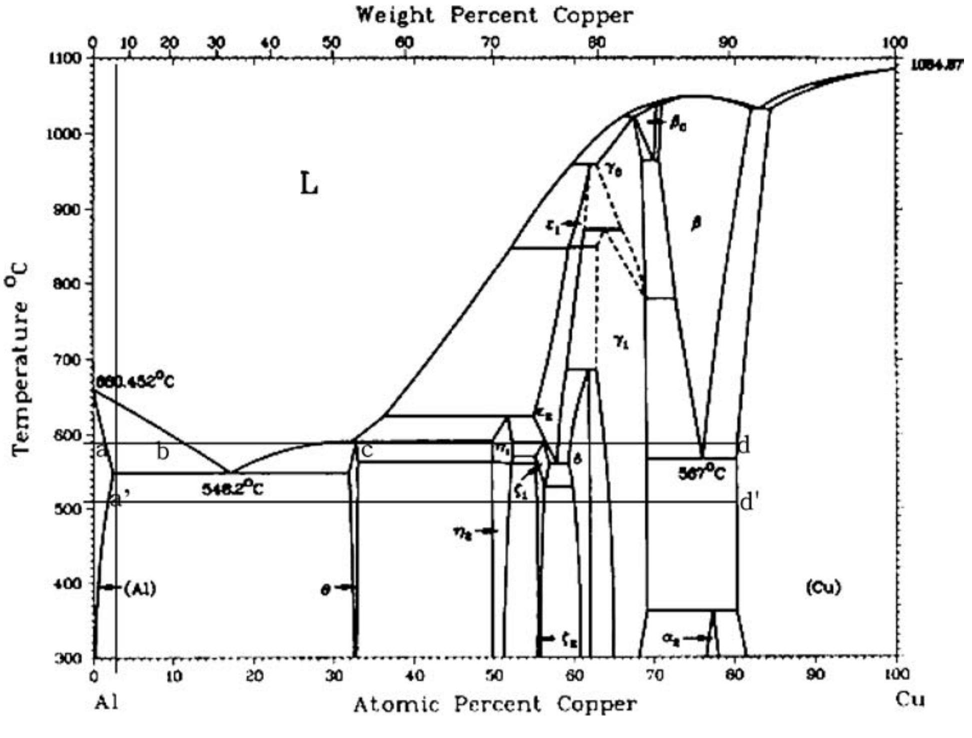

Figure 4 The Al–Cu phase diagram [15].

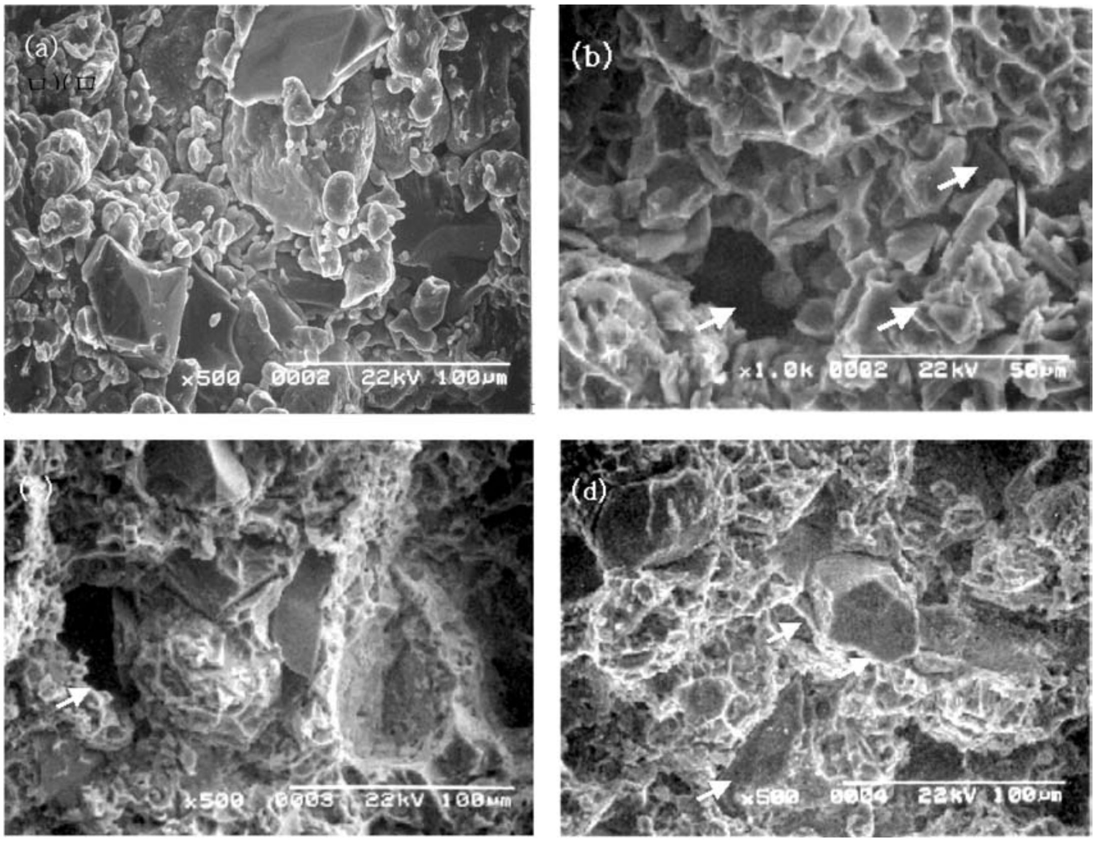

Figure 5 SEM fractographs of fracture specimens: (a) Al-44 μm SiC, (b) Al–Cu-8 μm SiC, (c) Al–Cu-44 μm SiC and (d) Al–Cu coated 44 μm SiC.

trends to the TRS, exhibiting the highest TS of 128 MPa with the copper-coated SiC particles. The large differences of the sintered strengths between the Al–SiC and Al–Cu–SiC composites demonstrate the effectiveness of the liquid phase for improving the bonding between the matrix powders and, also, with the SiC particles. The slightly higher sintered strength with the copper-coated SiC is probably due to the better void filling by the liquid phase around the SiC particles. In most particulate reinforced composites, finer reinforcing particles generally yield higher strengths, provided that they are uniformly dispersed. However, the sintered strengths obtained in the present study show the opposite result, that is, the finer 8 μm SiC particles in the sintered Al–Cu–SiC composite resulted in lower strengths than the coarser 44 μm ones. This is attributed to the larger agglomeration of the finer SiC particles and the associated voids as shown in the Fig. 2.

3.3. Fracture surface

The fractured surfaces were compared in Fig. 5 mainly for the tensile tested specimens since tension exerts a simpler state of stress on the specimens than bending. However, a bend tested specimen was examined for the Al–SiC$_p$ composites without copper since they were too weak and brittle to machine to the round tension specimens. The fracturing of sintered Al–SiC composite occurred predominantly along particle boundaries or interfaces with SiC with little indication of matrix deformation. The sintered Al–Cu–SiC composite was also fractured mainly along the boundaries or interfaces but with some matrix deformation. The sintered composite containing the finer 8 μm SiC were less deformed than those containing 44 μm SiC particles. Little difference is noted between the composites prepared from the mixed elemental Al–Cu–SiC and Al–copper coated SiC, even around the SiC particles. This indicates that the matrix powder boundaries and the interfaces along SiC particles are still weak areas despite the improved bonding by the liquid phase. The more brittle appearance associated with the finer SiC particles is also attributable to the agglomeration and voids, and possibly to the shorter spacings between the particles which can make the plastic deformation of the matrix in-between the particles more difficult [7].

4. Conclusions

Sintering behavior, microstructures and mechanical properties of mixed elemental Al–SiC, Al–Cu–SiC, and Al–copper coated SiC composites were investigated and explained in terms of the Al–Cu liquid phase formed during sintering and interfacial characteristics. The following conclusions can be drawn from this work:

(1) By adding 7.3 wt% copper to the mixed elemental Al-SiC, a sufficient amount of a persistent liquid phase was formed to fill most of the powder boundaries, pores in the matrix and some portion of voids associated with SiC particles.

(2) The liquid phase in Al–Cu–SiC resulted in an increase in density during the sintering and improved the sintered properties significantly. However, the alloying of copper in the aluminum matrix is restricted to less

than 2 wt% and the solidified liquid phase contains a large portion of brittle $CuAl_2$ phase. The boundaries bonded by the liquid phase still appear to provide easy fracture paths, indicating that further improvement should be made.

(3) The finer 8 μm SiC particles tended to agglomerate more than the coarser 44 μm SiC particles, causing lower sintered density and sintered strength, and a more brittle fracture appearance.

(4) Despite the improved void filling around SiC particles and a slightly more densification during the sintering by utilizing the copper coated SiC particles, the resulting sintered properties and the fractured appearance do not differ significantly from those obtained from the mixed elemental copper powders.

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References

1. N. V. RAVI KUMAR and E. S. DWARAKADASA, *Composites*, Part A **31** (2000) 1139.
2. C. SRINIVASA RAO and G. S. UPADHYAYA, *Mater. Design* **16** (1995) 359.
3. B. G. KIM, S. L. DONG and S. D. PARK, *Mater. Chem. Phys.* **72** (2001) 42.
4. I. OZDEMIR, U. COCEN and K. ONEL, *Comp. Sci. Techn.* **60** (2000) 411.
5. J.-C. LEE, J.-Y. BYUN, C.-S. OH, H.-K. SEOK and H.-I. LEE, *Acta Mater.* **45** (1997) 5303.
6. A. M. DAVIDSON and D. REGENER, *Comp. Sci. Techn.* **60** (2000) 865.
7. L. M. THAM, M. GUPTA and L. CHENG, *Acta Mater.* **49** (2001) 3243.
8. B. OGEL and R. GURBUZ, *Mater. Sci. Engng.* A **301** (2001) 213.
9. M. GUPTA, M. K. SURAPPA and S. QIN, *J. Mater. Proc. Techn.* **67** (1997) 94.
10. S. K. TAKUR and B. K. DHINDAW, *Wear* **247** (2001) 191.
11. C. A. LEON and R. A. L. DREW, *J. Mater. Sci.* **35** (2000) 4763.
12. W. S. CHUNG, S. Y. CHANG and S. J. LIN, *Plat. Surf. Finish.* **83** (1996) 68.
13. G. B. SCHAFFER, T. B. SERCOMBE and R. N. LUMLEY, *Mater. Chem. Phys.* **67** (2001) 85.
14. C. HU and T. N. BAKER, *Mater. Sci. Engng.* A **190** (1995) 125.
15. "Alloy Phase Diagrams, ASM Handbook" (ASM International, Materials Park, OH, 1992) Vol. 3.

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