Liquid phase sintering of an AA2014-based composite prepared from an elemental powder mixture

J. ZHOU, J. DUSZCZYK
Laboratory for Materials Science, Delft University of Technology, Rotterdamseweg 137, 2628 AL Delft, The Netherlands
E-mail: J.Zhou@stm.tudelft.nland, J.Duszczyk@stm.tudelft.nl

The AA2014 alloy reinforced with 10 vol % SiC particles has been prepared from elemental powders blended with the ceramic particles, instead of using a pre-alloyed atomized powder as the matrix material. Of critical importance in taking this uncommon processing route is liquid-phase sintering to transform the initial free aluminum and copper powder particles into the α-Al and the θ-phase, thereby producing an integrated structure. The present investigation looked into the effect of sintering parameter on the microstructure and mechanical properties of the composite. It is shown that a sufficient time of sintering in the presence of a small volume fraction of the eutectic liquid must be given to dissolve the free copper particles in the α-Al solid solution. However, a prolonged sintering time will lead to the thickening of grain boundaries. A fast cooling after sintering is necessary to avoid the formation of a layered structure at grain boundaries as a result of local sequential solidification. With an adequate sintering scheme, the composite can be successfully fabricated to attain a strength of over 440 MPa after the standard T6 heat treatment.
© *1999 Kluwer Academic Publishers*

1. Introduction

Materials and processing costs in many ways hold the key to the wide application of aluminum matrix composites in industry. One of the major factors causing the high costs of the composites prepared by powder metallurgy (PM) techniques is that the matrix alloy is often a costly high-strength pre-alloyed one prepared by inert-gas atomization. An additional disadvantage is that part of acquired conventional PM processing equipment for aluminum alloys would be left unused [1].

To explore the possibilities of preparing aluminum matrix composites which have enhanced properties and are affordable for industrial use, a processing route has been chosen that involves blending of an elemental powder mixture with SiC particles, cold compaction, liquid-phase-sintering in combination with dewaxing and degassing, and hot extrusion. Using elemental powders has cost advantages in both raw materials and processing because they are softer to be packed with each other and easier to hold the non-deformable reinforcement under low compacting pressures. Moreover, it makes it possible to change the matrix composition.

Obviously, in this processing route, liquid phase sintering is the key. It is commonly understood that sintering, typically at a temperature below the melting point, cannot be applied to establish the bonding of a packed aluminum powder, because a thermochemically stable oxide layer covering the powder particle surfaces prevents mass transport by diffusion to attain full structural cohesion. In a two-phase system, however, when the sintering temperature is above the eutectic temperature, the melt can penetrate the oxide layer at the cracks caused by compaction, undermine and finally lift off the oxide layer to produce interparticle bonding. One should, however, note that not all aluminum alloys or alloy compositions are suitable for liquid phase sintering, because the criteria that the generated melt must have a high wettability to and a high solubility in the solid phase must be satisfied. For an aluminum-copper powder mixture with an intended alloying composition of the AA2014 (Al–4.5Cu), when the sintering temperature is higher than the eutectic temperature (548 °C), the Al-Cu$_2$Al (θ-phase) eutectic is formed at the interfaces of the neighboring aluminum and copper powder particles. As sintering proceeds, the interfaces move by dissolving the copper powder particles in the aluminum powder particles from the melt and at the same time consuming the copper powder particles into the melt. When the volume fraction of added SiC particles is not too high, the process of mass transport during liquid phase sintering should not be interfered with to a large extent. Furthermore, the formed eutectic melt may attack the surfaces of SiC particles to remove surface contaminates and to create crystallographic facets [1], which provides good mechanically interlocked interfaces, important to the wear resistance and the tensile properties of the composite material.

The aim of the present work was to verify the above sintering theory and to optimize the liquid phase sintering in order to exploit the potential strength of the composite.

2. Experimental procedure

The as-received raw material used as the matrix of the composite was a powder mixture with a nominal composition corresponding to the AA2014 alloy, i.e. 4.5% Cu, 0.7% Si, 0.5% Mg and the balance aluminum. The mixture had a median size of 95 μm and was added together with 1.5 wt % Microwax C to facilitate compaction in and ejection from the die prior to sintering. The as-received reinforcement was a SiC powder with a median size of 23 μm. The SiC addition was 10% by volume.

The matrix powder mixture was blended with the SiC particles using a Sartorius 1213HP turbula mixer at a rotation speed of 42 r.p.m. for 30 min. The service container had a volume of 1 l and was loaded with 30% of the volume. The blended feedstock had an apparent density and a tap density of 1.0–1.1 and 1.3–1.4 g cm^{-3}, respectively. It was then cold compacted in a steel die with an internal diameter of 49.4 mm using a single-action, uniaxial press at a load of 290 kN corresponding to 151 MPa. The compacts weighed 150 g each.

In order to minimize the processing costs, the de-waxing, degassing and sintering were combined into a single operation, i.e. dewaxing at 420 °C for 25 min and degassing during heating up from 420 to 590 °C with a duration of 30 min prior to sintering. A pure nitrogen atmosphere was maintained throughout the cycle in a sintering oven.

Sintering parameters (temperature and time) are of decisive importance for the quality and properties of the PM products. At a temperature below the eutectic temperature (548 °C) of the Al–Cu system, diffusion in the solid state is very slow, as stated earlier, and as a result strong bonding between the elemental aluminum and copper powders cannot be established. Above this critical temperature, the liquid eutectic phase appears at the boundaries between the neighbouring aluminum and copper particles. When the temperature is a few degrees higher, e.g. 550 °C, only a very small proportion of liquid exists for a short time, because the matrix alloy on the whole falls in the area of the α-Al solid solution [2]. In this case, sintering cannot be completed. To maintain a certain proportion of liquid, sintering must be carried out in the solidus-liquidus area of the Al–Cu system, i.e. above 570 °C for the AA2014 alloy. Too high a temperature will, however, lead to a very large proportion of liquid because of the gentle slope of the liquidus, to a potential of shape changes of the compacts and also to the coarsening of the α-Al grains and the θ-phase at grain boundaries. Based on the above sintering theory applied to the Al–Cu system, a sintering temperature of 590 °C was chosen where about 6 wt % of liquid could be maintained. Sintering time is the second variable of the process. In the present investigation, it varied from 30 to 90 min to determine an appropriate duration for producing a satisfactory combination of strength and ductility of the composite. After sintering, the composite in a compartment with nitrogen flowing through was taken out of the furnace to let the compartment cool in air till room temperature was reached. For comparison purposes, the sintered compacts were also allowed to cool at a much slower rate in the sintering oven.

The sintered compacts had a porosity of about 19.3 % and their inherent mechanical properties were not fully developed. Hot extrusion was used a means of consolidating the material at 450 °C, a reduction ratio of 40 : 1 and an exit speed of 19–20 m min^{-1}. The extruded bar was subjected to stretching to a strain of 1%. Finally, the standard T6 heat treatment was applied to the extruded bars, which consisted of a solutionizing at 490 °C for 30 min followed by cooling in water and an ageing at 160 °C for 18 h.

3. Results and discussion

After cold compaction under a pressure of 151 MPa, the compacts were found to be sound enough for handling, indicating that deformation had occurred to provide interlocking between the metal powder particles where SiC particles were caught in between. After being ejected from the die, the compacts expanded radically from 49.40 to 49.85 mm in diameter. Their average green density was 2.358 g cm^{-3}, i.e. 83.60 % of the theoretical density (which is 2.823 g cm^{-3} according to the rule of mixtures). Due to the presence of the non-deformable SiC particles in the feedstock, the achievable relative density was decreased under the given pressure (the relative green density of the material without SiC particles was 86.21%). A relative green density below 85% could yet provide interconnected channels for the vaporization of the wax during subsequent dewaxing and for the evaporation of physically adsorbed moisture and decomposed hydroxides on the metal powder surfaces during degassing prior to sintering.

After sintering at 590 °C for 30–90 min, the shape of the compacts remained cylindrical. However, their average weight decreased from 150.0 to 148.5 g, which was apparently caused by the removal of the lubricant (1.5 wt %). The compacts had a slight swelling in the axial and radical directions (1.8% and 0.30%, respectively). The differences in dimensions between the compacts sintered for the different times were not measurable. The average sintered density was measured to be 2.278 g cm^{-3}, i.e. 80.69% relative to the theoretical density, and thus the densification parameter of sintering [3] could be calculated to be −0.177. This negative value shows an interesting behavior of the matrix material prepared from the elemental powders. The loss of the weight of the compacts due to the release of the wax is certainly a contributing factor. However, the observed increases in the length and diameter of the compacts are also an important factor. Because the sintering temperature used in the present experiments was relatively low and only a small proportion of liquid (6% by weight) was generated, rearrangement of the metal powder particles and SiC particles to result in shrinkage of the compacts could not

TABLE I Mechanical properties of the composite after sintering, extrusion and heat treatment

Material	As-sintered hardness (Brinell at 0.25 kg)	As-extruded		As-heat-treated	
		Strength	Elongation	Strength	Elongation
30 min sintered composite	38.6–50.1	318.5 MPa	7.5%	391.3 MPa	3.4%
60 min sintered composite	36.3–43.7	308.2 MPa	6.9%	445.6 MPa	3.1%
90 min sintered composite	36.6–44.4	305.9 MPa	9.3%	442.9 MPa	2.6%

be significant enough to overcome the swelling caused by the solution of copper in the α-Al and the penetration of the eutectic melt along the grain boundaries. Moreover, the presence of the SiC particles would inevitably obstruct the rearrangement of the metal powder particles for shrinkage. This explanation is supported by the fact that the relative sintered density of the compacts without the SiC particles was slightly higher (81.94%).

After sintering, the compacts had an enhanced soundness thanks to structural cohesion, but they did not yet possess their full strength. This is indicated by the wide variations of the measured green hardness of the compacts (Table I), which were caused by the pores remaining in the sintered compacts.

Although the sintered density appeared to the same for the compacts sintered for different times, microscopy showed a decreased porosity level with increasing sintering time, as can be seen from Fig. 1. This is probably associated with the time available for the rearrangement of the solid-phase particles coexisting with the melt. The micrographs also show the homogeneous distribution of the SiC particles which are mostly situated in the triple junctions of the grain boundaries. Most of the pores are associated with the SiC particles which could obstruct the rearrangement of the matrix particles during sintering.

The as-sintered microstructures are shown in Fig. 2. It is clear that after 30 min sintering, the structure is composed of the α-Al and the θ-phase at grain boundaries and in the grain interior, in addition to the SiC particles and pores. Those in the grain interior were precipitated during the cooling in the solid state (the secondary θ-phase), as the solubility of copper in the α-Al decreased progressively with decreasing temperature. Those at the grain boundaries were degenerated from the eutectic reaction originating from the free aluminum and copper particles. During sintering, the eutectic melt and the θ-phase were first formed by dissolving the packed aluminum and copper particles. The diffusion of copper through the melt into the aluminum occurred preferentially along the grain boundaries.

During sintering at 590 °C for 30 min, the equilibrium solubility of copper in the α-Al, about 3.6%, might not yet have been reached. The θ-phase transformed from the free copper particles, especially the large ones, would still remain behind in the liquid phase. During subsequent cooling, the new θ-phase formed at grain boundaries through the degenerated eutectic reaction. The presence of a large number of the discrete θ-phase particles at grain boundaries (see Fig. 2a) led to a net-

work in which cracks would easily propagate. As the subsequent extrusion and heat treatment could not completely eliminate this network, the mechanical properties of the material were degraded, as will be shown later.

After 60 min sintering, more diffusion could be expected to have occurred and the grain boundaries would be more depleted of the coarse θ-phase particles, as can be seen in Fig. 2b. The existing θ-phase was mostly formed due to the degeneration of the eutectic reaction, as will be discussed below.

In the material sintered for 90 min, the grain boundaries are slightly thickened (to as much as about 1 μm) containing the θ-phase in the forms of particles and layers (Fig. 2c). It may be understood that after staying at that temperature for so long, the structure of the material consisting of the α-Al and the melt, in addition to the SiC particles and pores, approached the equilibrium compositions. The melt situated in the grain boundaries through penetration would attack the α-Al. During subsequent cooling, solidification at the grain boundaries proceeded by gradually forming the α-Al with the compositions closely corresponding to the solidus, on the initial α-Al grains. The remaining liquid was then enriched with copper to reach the eutectic composition and solidified at 548 °C with first formation of the θ-phase and then the α-Al (degeneration of the eutectic). This may explain the thickening of the grain boundaries due to a prolonged sintering time. It should be noted that in the present experiments, since cooling from the sintering temperature to the eutectic temperature was very fast, the layering of the phases at the grain boundaries did not fully develop to such an extent as to influence the mechanical properties of the sintered material. However, if the composite was left to cool in the sintering oven at a very low cooling rate, the grain boundaries would be greatly thickened with the layering θ-phase and α-Al phase as a result of the sequential phase transformations. At the beginning of slow cooling, the α-Al would solidify along the existing α-Al grains from the melt at the grain boundaries. As uniquely happens in the Al–Cu system, the subsequent eutectic reaction would degenerate into the θ-phase as the eutectic origin (similar to the primary θ-phase formation) and finally the remaining liquid would solidify on the surfaces of the existing grains. Such a recast structure at the grain boundaries transformed from the melt was found to greatly reduce the strength of the material.

It was noted that the presence of the SiC particles in the material did not influence the sintering behavior of the matrix elemental powders, although a
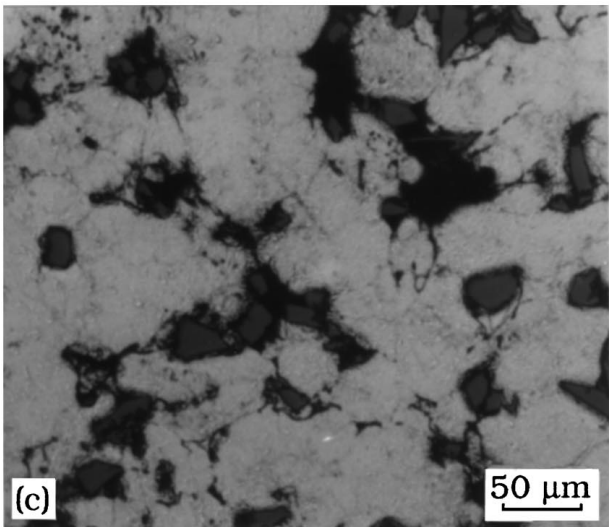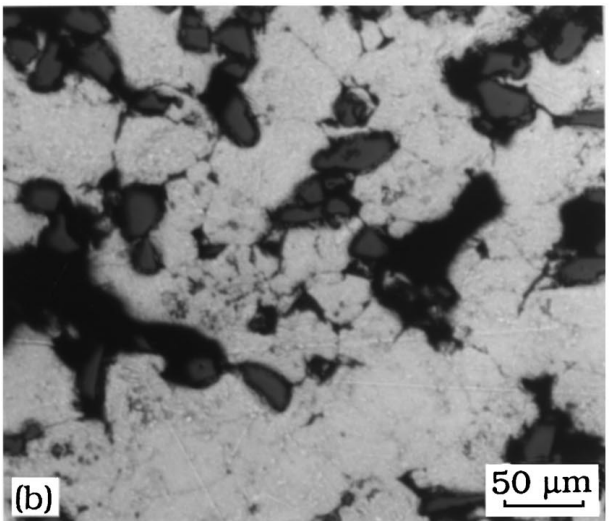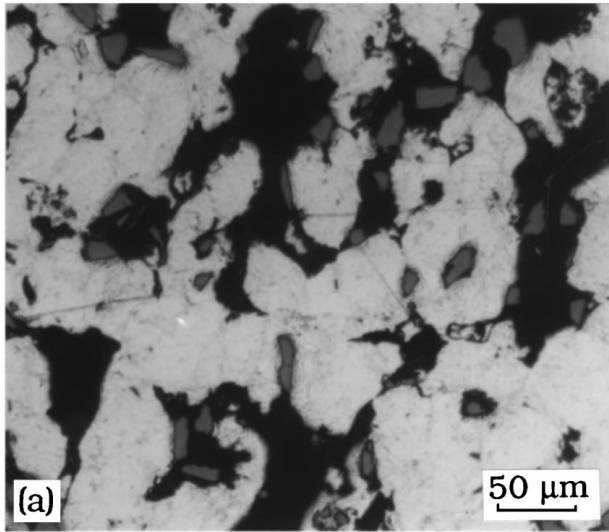
Figure 1 Microstructures of the composite sintered for (a) 30 min, (b) 60 min and (c) 90 min, showing the SiC particles and pores.
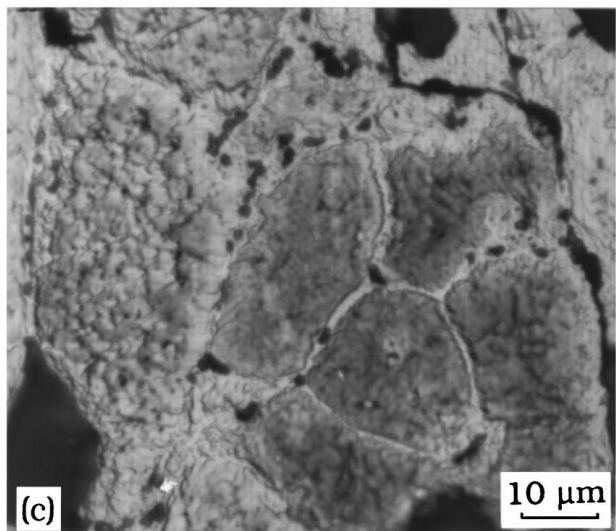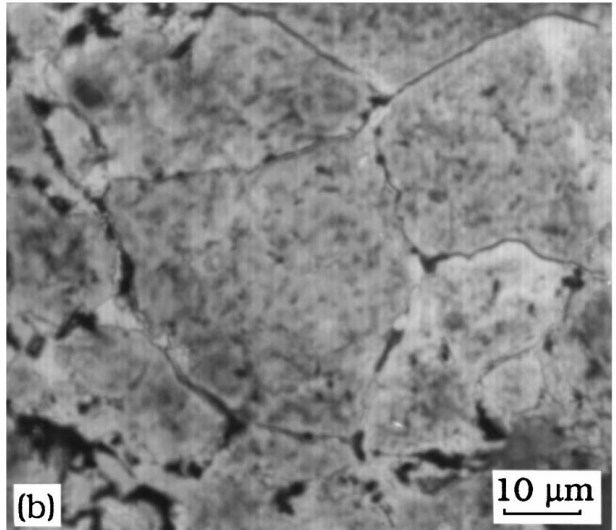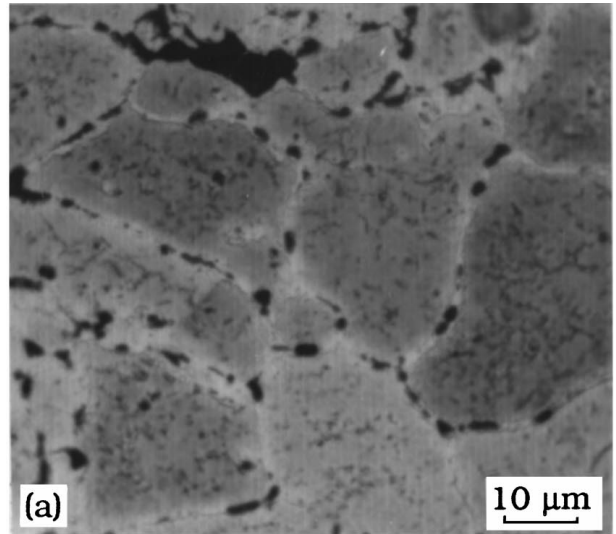

Figure 2 Microstructures of the composite sintered for (a) 30 min, showing the large discrete θ-phase particles at the grain boundaries, (b) 60 min, showing the depletion of the θ-phase particles at the grain boundaries and (c) 90 min, showing the thickened grain boundaries.

few free copper particles that were entrapped in the clusters of SiC particles and thus lost direct contact with the aluminum particles could be expected to remain undissolved. Optical microscopy could not reveal any interactions between the SiC particles and the melt occurring at the sintering temperature. However,

it has been observed with electron microscopy that in the presence of the liquid, SiC particles would be attacked to form facets along the $(0\,0\,0\,1)$ and $(1\,1\,2\,0)$ planes [1].

Figure 3 (a) Transverse and (b) longitudinal microstructures of the composite after 30 min sintering and extrusion.
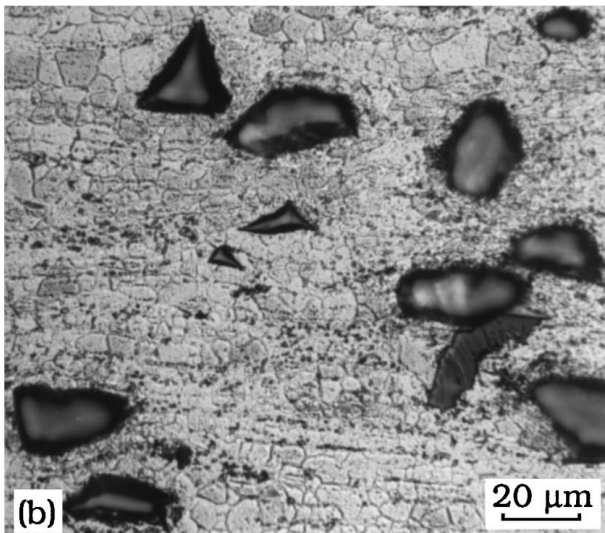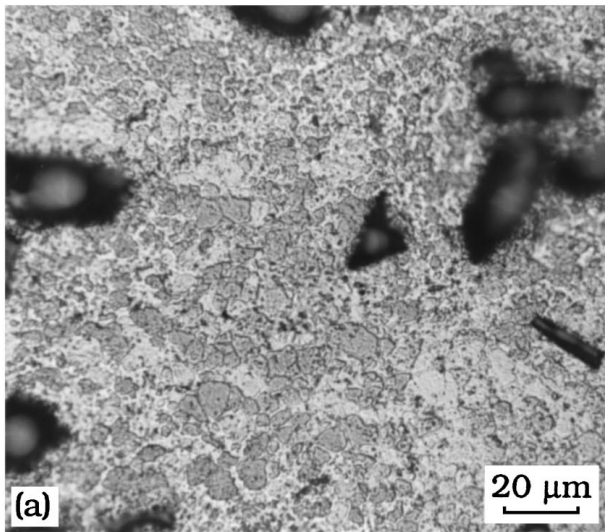

Figure 4 (a) Transverse and (b) longitudinal microstructures of the composite after 60 min sintering and extrusion.

After extrusion, the composite was fully densified and had a good surface finish. Figs 3, 4 and 5 show the as-extruded microstructures of the material in the transverse and longitudinal sections. There is no substantial difference in microstructure between the material sintered for the different times. In the transverse sections, the SiC particles are uniformly dispersed in the matrix with a mean grain size of about 5 μm. In the longitudinal sections, they are well aligned in the extrusion direction, indicating that the SiC particles experienced rotation and rearrangement, due to the severe shearing involved in extrusion deformation. No cracking of SiC particles was found.

In comparison with the grain structure of the sintered material shown in Fig. 2, it is clear that the initial grains have been greatly elongated after extrusion. This can be seen from the longitudinal microstructures of the extruded material, containing well-developed equiaxial subgrains. The grain alignment along the metal-flow direction of extrusion would be disturbed by the nondeformable SiC particles that forced the matrix material to flow around them. The thickened grain boundaries produced during prolonged sintering were reshaped during extrusion, but the characteristics of the grain boundaries in the matrix of the composite largely remained (see Fig. 6).
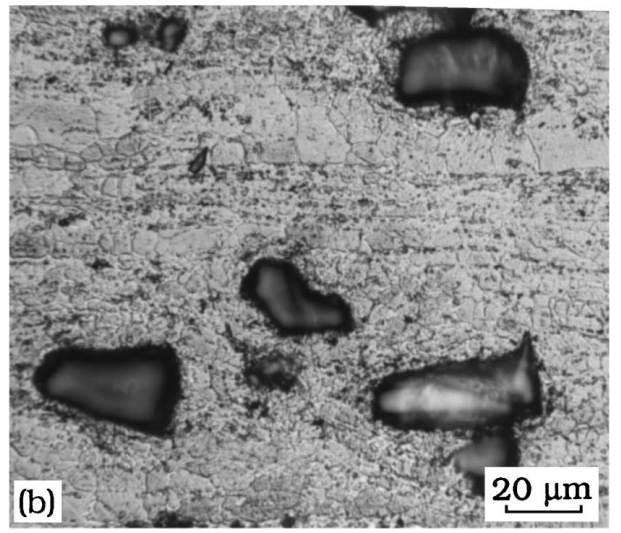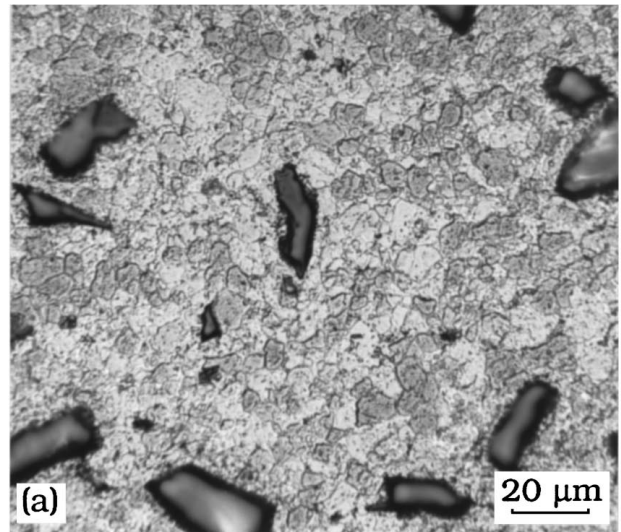
Heating of the material to 450 °C prior to extrusion deformation would bring part of the precipitated θ-phase back into the α-Al solid solution. During cooling after extrusion, re-precipitation would take place and the new precipitates would be associated with subgrain boundaries within the grains. It should be noted that this re-precipitation could well be avoided by using press-quenching, as is common practice in the aluminum extrusion industry. With the correct control of extrusion parameters, mainly billet temperature, ram speed and reduction ratio, the exit temperature of the material can fall in the range of 490–500 °C. As a result, the subsequent solutionizing would not be necessary and the subgrain structure could be retained, which would contribute to the matrix strength. In such a way, the processing costs could be cut.

The ultimate tensile strength and elongation of the composite material sintered for the different times in the as-extruded and as-heat-treated conditions are given in Table I. In general, the T6 heat treatment significantly increased the strength of the composite at the cost of tensile ductility. This indicates the decisive role of the
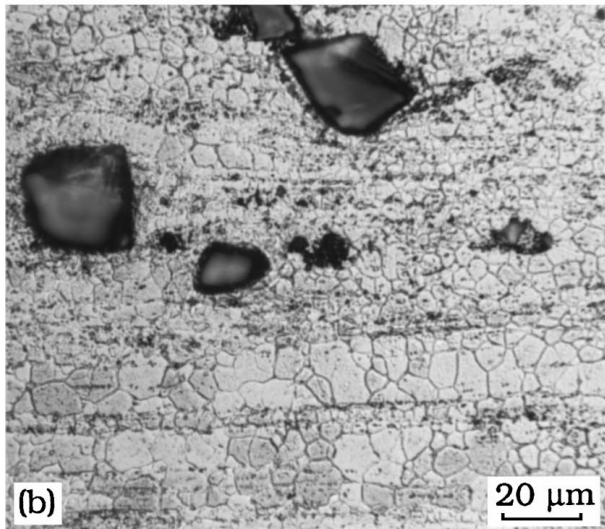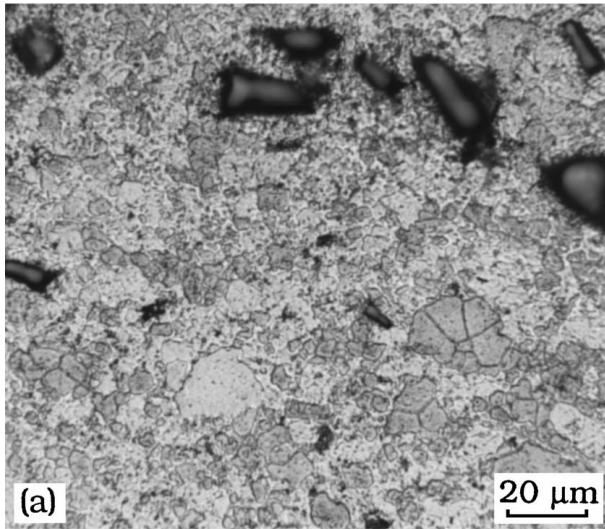
549

Figure 5 (a) Transverse and (b) longitudinal microstructures of the composite after 90 min sintering and extrusion.
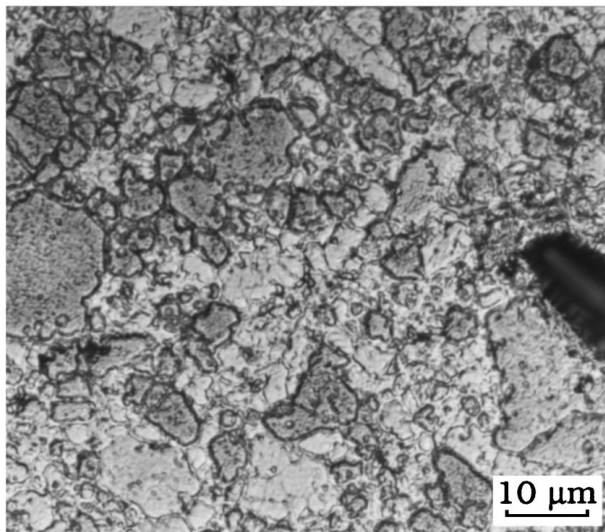

Figure 6 Microstructure of the composite on the transverse section after sintering for 90 min and extrusion, showing the remaining thickened grain boundaries in the matrix.

matrix structure (with the θ''-phase and θ'-phase induced during ageing) in determining the mechanical properties of the composite. It is clear that sintering at 590 °C for 60 min produces the best combination of strength and elongation. Obviously, the tensile properties of the composite are largely governed by the grain size and the distributions of the precipitates and SiC particles. The lower strength of the material sintered for 30 min was probably caused by the incomplete dissolution of the copper-rich particles and insufficient diffusion of copper in the α-Al to attain the maximum solubility at the sintering temperature of 590 °C. The T6 heat treatment (during which diffusion in the solid state would occur) could not fully compensate for the shortage of sintering time. For the composite sintered for 90 min, the slightly thickened grain boundaries with the θ-phase particles may be responsible for the lower strengths both in the as-extruded condition and in the as-heat-treated condition. The same material slowly cooled in the sintering oven after sintering had a strength of 80 MPa in the as-extruded condition and a strength of 220 MPa in the as-T6-tempered condition. The decreases in strength are attributed to the thickening of the grain boundaries and the layered structure in the boundaries.

4. Conclusions
The present investigation confirms that liquid phase sintering is a viable processing step in preparing the AA2014-based composite containing 10 vol % SiC particles from an elemental powder mixture. The strength achievable is as high as 440 MPa after the standard T6 heat treatment. Sintering time influences the mechanical properties of the composite and a holding time of 60 min at 590 °C is found to be sufficient for interdiffusion of aluminum and copper to form the α-Al and θ-phase without much interference of SiC particles. However, an excessively long sintering time would decrease the strength of the composite, especially together with slow cooling after sintering.

References
1. S. J. YANKEE, G. M. JANOWSKI and B. J. PLETKA, *Mater. Manuf. Process.* **5** (1990) 147.
2. L. F. MONLDOFO, in "Aluminum Alloys: Structure and Properties" (Butherworths, London, 1976) p. 253.
3. R. M. GERMAN, in "Powder Metallurgy Science," 2nd Edn (Metal Powder Industries Federation, New Jersey, 1994) p. 243.