Spray forming of ultra-fine SiC particle reinforced 5182 Al-Mg

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This paper describes the spray forming of SiC particle reinforced Al metal matrix composites (MMCs) with particular emphasis on microstructure characterization of SiC particle distribution. A 5182 Al-Mg alloy was used as matrix material, and SiC particles with a mean diameter of 1.2 μm and 2.0 μm as reinforcement. The reinforcing particle distribution and microstructural characteristics of MMCs were analyzed in the current study using TEM, SEM and optical microscopy. The distribution of SiC particles in the as-spray deposited and hot-extruded conditions was characterized. SEM results indicate that the SiC particles are homogeneously distributed although some clustering was evident in the matrix. TEM and OM examinations show that most of SiC particles are present intergranularly in the Al matrix. EDS analysis indicated that Mg tends to segregate and form oxide phases in the vicinity of SiC particles and that there is no compositional variation of Mg across grain boundaries in the Al matrix.

1. Introduction

Spray forming has been applied for manufacturing particle reinforced metal matrix composites (MMCs) for about one decade, and has attracted attention in recent years with the in-depth understanding of the process fundamentals involved in spray forming. Ideally, metal matrix composite materials would combine the properties of metallic matrix materials (toughness and ductility, in general), and those of reinforcement phases (high strength, stiffness and thermal stability). Conventional techniques of manufacturing metal matrix composites include squeeze casting, stir casting, mechanical alloying, and the blending of particles with metallic powders [1, 2]. However, inhomogeneous distribution (segregation) of reinforcement particles as well as chemical reaction between melt and reinforcement phase, associated with these conventional methods, will inhibit the full potential applications of particle reinforced metal matrix composites [3]. In addition, powder metallurgy approach (blending method) needs extra procedures for consolidation, such as rolling, extrusion, solid phase sintering etc. [4]. Spray forming, which combines rapid solidification characteristics and near-net-shape manufacturing of materials, was developed as an alternative to the conventional techniques as mentioned above. Co-injection of reinforcements during spray forming can introduce reinforcing particles into metallic matrices. In principle this co-deposition technique can reduce or eliminate the extreme thermal excursions which may result in interfacial reaction and extensive macrosegregation of reinforcements as well as porosity formed during slow solidification that normally exist in the conventional fabrication of MMCs. This will in turn improve the mechanical properties of MMCs [5, 6]. An extensive review of the spray forming of MMCs is available elsewhere [6]. It has been reported [1] that the volume fraction of particle up to 20–25% can be successfully incorporated using spray atomization and co-deposition technique. Inspection of literature finds that the mean diameter of particles is normally in the range of 5–20 μm [2, 7–10].

Thermomechanical processing including conventional forging, extrusion and rolling is generally applied to modify the microstructure of conventionally manufactured MMCs for improving mechanical properties, and/or to form the material to an end-use product shape [11]. As MMCs generally demonstrate low tensile ductility and poor toughness at room temperature, and limited tensile ductility at elevated temperature, conventional fabrication techniques are relatively difficult for complex mechanical shaping [12]. It is well documented [11–14] that Al-based and Mg-based

MMCs show superplasticity. Superplastic forming is an attractive alternative for shaping MMC materials. In superplastic forming, one important microstructural requirement is fine-grain feature that is typically about 10 μm or less. Since it is generally believed that grain boundary sliding is responsible for superplastic deformation, fine-grain feature can provide the short distances which facilitate slip and diffusional accommodation of strain incompatibility among grains, and avoid or delay the cavity formation. It is well accepted that superplastic strain-rate varies inversely with grain size. As the grain size decreases, the superplastic flow rate increases. Achievement of such a fine-grain structure has led to the discovery of one important and interesting phenomenon, high strain rate superplasticity (HSRS) demonstrated by MMCs [15]. Compared to the conventional superplastic forming rate (approximately 10^{-4} s^{-1}), high strain rate superplasticity can be carried out at much higher rates (normally 10^{-1}–10^{2}) [13]. High strain rate superplasticity can make materials undergo superplastic forming at high deformation rate, and this is desirable for production of large quantities of parts economically [11, 13]. Compared to the MMCs by conventional fabrication methods such as ingot metallurgy (I/M) or powder metallurgy (P/M), those made by spray forming technique necessitate less processing steps to achieve the fine-grain structure. This is attributed to the fact that spray forming can form fine grains resulted directly from the rapid solidification of the melts, generally saying, in the range of 30–50 μm [6], whereas the starting grain size is generally larger than 150 μm for materials processed by I/M method [16].

Homogeneity of particle reinforcements in the matrix is another important factor that influences the superplastic behavior, mechanical properties, and afterward the performance of MMCs. In general, the reinforcing particles are more or less non-uniformly distributed (particle clustering) in the metal matrix materials. Particle clustering and the resultant local inhomogeneity is one of the detrimental factors to the performance of particle reinforced MMCs, and is resulted from the manufacturing processes [17]. In I/M processing, the reinforcing particles may be pushed or engulfed by the advancing solidification front. During solidification, the liquid/solid front may become instable and break down into cell, dendrite, or equiaxed grain structure. In this case, the particles, if pushed at the liquid/solid interface, may be entrapped at the end of local solidification, resulting in the formation of particle clustering. The solidification rate is an important parameter in determining if the particle clustering occurs. At lower rate, the advancing solidification front pushes the particles along continuously, leading to an increase in the particle clustering [17–19]. It is well documented [20, 21] that however, increasing the advancing solid/liquid front rate changes the particle behavior from pushing to entrapment. In P/M method however, particle clustering may be formed due to: (1) the fine particles remain in agglomeration at the blending and mixing stage for making composites [17]; and (2) the relatively coarse alloy powders used in the initial composite consolidation stage [22]. It is worthy noting that P/M processed composites show a more homogeneous microstructure, that is less pronounced particle inhomogeneous distribution, than I/M composites. With respect to the influence of the particle clustering on the performance of MMCs, it has been reviewed [17] that such kind of local inhomogeneity promotes the tendency of void nucleation, growth, and coalescence. In general, deformation often occurs inhomogeneously in composites with a non-uniform distribution of the reinforcing particles. Plastic deformation is often initiated in those microstructural regions with a low concentration of particles, whereas in those regions with a high particle density, initiation and growth of cracks are more favorable to occur resulting in low fracture toughness [23]. This was evidenced by experimental results of SiC particle reinforced Mg matrix composite that cavities formed in association with SiC agglomeration where the local stresses were escalated [24]. As described before, thermomechanical processing is an important step to modify the microstructure of conventionally manufactured MMCs, and accordingly for improving mechanical properties. However, there are some existing problems resulted from thermomechanical processing, such as particle/matrix decohesion or particle fracture. Typically, decohesion occurs for very fine size of particles in P/M made MMCs due to relative weak interface between particle/matrix. Large particles, for example greater than 10 μm however, are more prone to fracture during thermomechanical processing.

Another interesting phenomenon in MMCs is the influence of the reinforcing particles on the refinement of grain size of matrix materials. The solid reinforcing particles can reduce the grain size of the matrix when they act as heterogeneous nucleation catalyst for the matrix metal phase. A higher volume fraction of the reinforcing particles would result in a finer grain size due to more nucleation sites. However, the effects of particles on the grain size is generally evaluated with the Zener limitation, indicating the maximum achievable grain size due to the effect that particles exhibit in reducing grain boundary mobility [17].

In order to approach the superplastic forming of MMCs by spray forming, very fine reinforcements should be incorporated into the metal matrix for accommodation of microstructural requirement. However, co-injection of very fine particles (i.e., a few micrometers in size) is typically avoided as a result of the following issues: (i) strong tendency to agglomerate during processing, which limits mechanical performance; (ii) high reactivity of fine particles which can lead to undesirable interfacial reactions; (iii) high cost associated with fine particles which requires a high yield during fabrication in order to maintain economic feasibility and (iv) the lack of fundamental information related to the behavior of MMCs that are reinforced with fine particles. Accordingly, in the present investigation, co-injection of ultra-fine SiC particles with mass median diameter of 1.2–2 μm was introduced to produce Al metal matrix composites. Distribution of SiC particles in the matrix as well as the interfacial regions between matrix and SiC particles were characterized. The influence of thermo-mechanical processing (extrusion herein) on the distribution of SiC particles was also investigated.

2. Experimental procedures

Fig. 1 presents a schematic diagram showing the spray forming used in the present study. A 5182 Al-Mg alloy (Al-4.5% Mg-0.35% Mn) was selected for the synthesis of MMCs reinforced by ultra-fine SiC particles. For the atomization of the matrix materials, the master alloys were remelted and superheated to temperatures of 150 K above the equilibrium liquidus, and maintained for 15–20 minutes to ensure uniform temperature of melts. The melts were then atomized into a distribution of micrometer-size droplets using high velocity nitrogen gas jets. To reduce oxidation, the experiments were conducted inside an environmental chamber, which was evacuated and backfilled with nitrogen to a pressure of 1.05×10^5 Pa prior to melting and atomization. As a distribution of atomized droplets traveled towards a water-cooling substrate for deposition, SiC particles were injected into the metal spray cone using a coaxial injector, designed on a fluidized bed principle. In the present studies, two types of ultra-fine ceramic particles of α-SiC were used for co-injection into the matrix materials. First size distribution is designated as UF 1.2, hereafter, and exhibits a volume median diameter of 1.1 μm and 3% volume of particles which are larger than 5 μm. Second one is designated as UF 2.0, and exhibits a volume median diameter of 2.0 μm and 3% volume of particles which are larger than 6 μm.

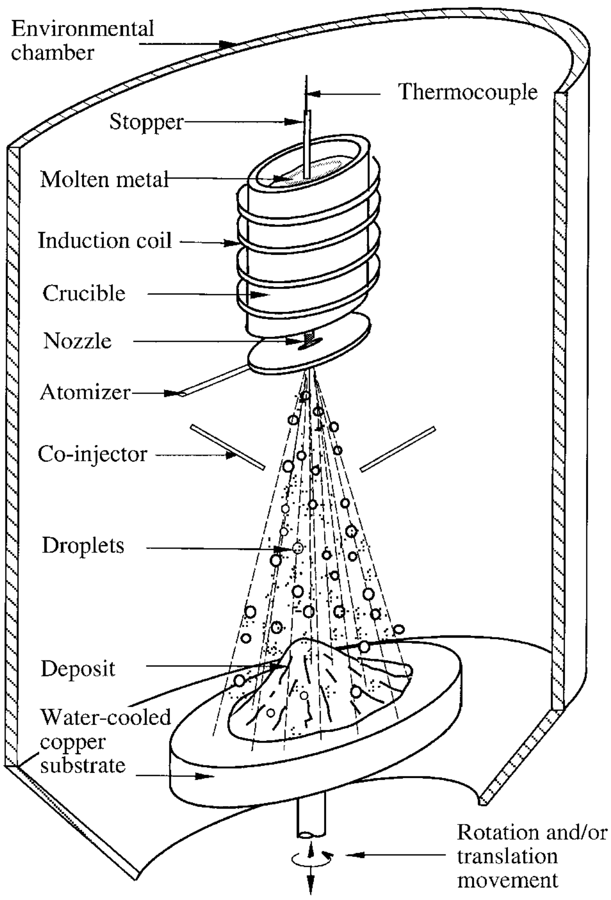

Figure 1 A schematic showing spray forming and co-injection deposition.

In order to compare the influence of SiC particle size on the spatial distribution characteristics, a larger size of SiC particles, with a volume median diameter of 9.0 μm, was also used in the present work. The matrix material used for these studies was a Al-4.5% wt. Cu binary alloy.

In the co-injection of SiC particles, high pressured nitrogen was used and regulated to the desired pressure as gas source into the injector. In general, increasing the fluidization pressure can result in an increase in the mass flow rate of SiC particles. This is attributed to the fact that increasing the fluidization pressure results in an increase in the volumetric gas flow rate of the carrier gas. In the present study, inlet gas pressure for injection of fine SiC particles was used as 0.38 MPa (55 psi). The co-injection angle was chosen as 80 degree.

Hot extrusion was used to reduce the micrometer-sized porosity generally associated with spray formed materials [25], as well as to modify the microstructure of the sprayed materials [16]. The samples of the as-spray deposited Al/SiC_P materials were sectioned and fabricated into 25.4 mm (1.0″) diameter of billets and then hot extruded at 400°C in an extrusion area reduction ratio of 16 : 1. In the present study, effort was devoted to understanding of the effects of hot extrusion on elimination of the porosity in the spray formed MMCs, and distribution of SiC particles in the matrix materials. In addition, a specimen was extruded at 320°C with the same area reduction ratio in order to provide some insight into the influence of extrusion temperature on the resultant microstructure.

The volume fraction of SiC particles present in the spray formed MMCs was determined by chemical dissolution, followed by filtering to separate the SiC particles. To dissolve the sample, a solution of 37.5% hydrochloric acid (HCl) was used. The SiC particles were dried in a vacuum furnace and the volume fraction (V_f) was calculated from the following equations:

$$V_f = \frac{\left(\frac{W_{SiC}}{\rho_{SiC}}\right)}{\left(\frac{W_{MMC}}{\rho_{MMC}}\right)} \quad (1)$$

and

$$\rho_{MMC} = \frac{W_{MMC}}{\left[\frac{W_{MMC} - W_{SiC}}{\rho_{matrix}} + \frac{W_{SiC}}{\rho_{SiC}}\right]} \quad (2)$$

where W_{SiC} and W_{MMC} are the weight of the filtered SiC particles and the spray deposited MMC sample, respectively, ρ_{SiC}, ρ_{MMC}, and ρ_{Matrix} are the density of SiC particle, MMC sample and aluminum alloy matrix, respectively.

As-spray formed and as-extruded samples were examined under optical microscopy. A modified Poulton's regent was used: 50 mL Poulton's regent (12 mL HCl (conc.), 6 mL HNO_3 (conc.), 1 mL HF (48%), and 1 mL H_2O), 25 mL HNO_3 (conc.), 40 mL of solution of 3 g chromic acid per 10 mL of H_2O. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were also used to characterize the morphology and distribution of SiC particles in the Al matrix as well as the matrix microstructure.

3. Results

Following co-injection of reinforcing particles during spray forming, the distribution of SiC particles in the matrix necessitates a further characterization, since it affects the thermo-mechanical processing and the mechanical properties of the spray formed MMCs. This is due to that for fine particles, they have less mass momentum for injection and are easy to agglomerate compared to large particles. Fig. 2 shows SEM images of the as-deposited microstructure, indicating a homogeneous SiC particle distribution in the matrix of 5182 Al-Mg alloy. It can be seen, however, that agglomeration of SiC particles, to some extent, is present, which was related to co-injection of very fine particles less than 10 μm in diameter. The as-extruded microstructures are shown in Figs 3 and 4, parallel to the extrusion direction and perpendicular to the extrusion direction, respectively. Banded structure of SiC particles is evident in Fig. 3. Figs 5 and 6 reveal SiC clustering (agglomeration) in the as-deposited and as-extruded conditions, respectively. Voids are sometimes associated with these clusters, shown in Fig. 5b.

TEM observations of both as-deposited and as-extruded samples indicated salient microstructural features associated with the processing history. Fig. 7 shows typical distributions of SiC particles in the Al matrix for: (a) the as-deposited composite, and (b) the composite viewed normal to the extrusion direction. The size of the SiC particles varies from -0.2 μm to -2 μm and their shapes are irregular. Particles were situated both along grain boundaries and near to grain boundaries. Larger SiC particles tended to be intergranular, while smaller SiC particles were both inter- and intragranular.

Fig. 8 presents a comparison of SiC particle distribution both in perpendicular to and parallel to extrusion direction. The SiC particles tended to become oriented parallel to the extrusion direction as shown in Fig. 8b. However, as shown in Fig. 8a, no such alignment is evident in samples in perpendicular to the extrusion direction.

Fig. 9 shows two dark field images from as-extruded samples sectioned parallel (a) and perpendicular (b) to the extrusion direction, respectively. A common feature in both images is that there is some type of interface structure in the vicinity of SiC particles. EDS spectra, taken from the interface regions and shown in Fig. 10, indicate Mg enrichment in the vicinity of the SiC particles. The oxygen content is also higher in this area than in matrix. The spectral data lead to prediction that Mg tends to form an oxide at the interface between SiC and the Al matrix.

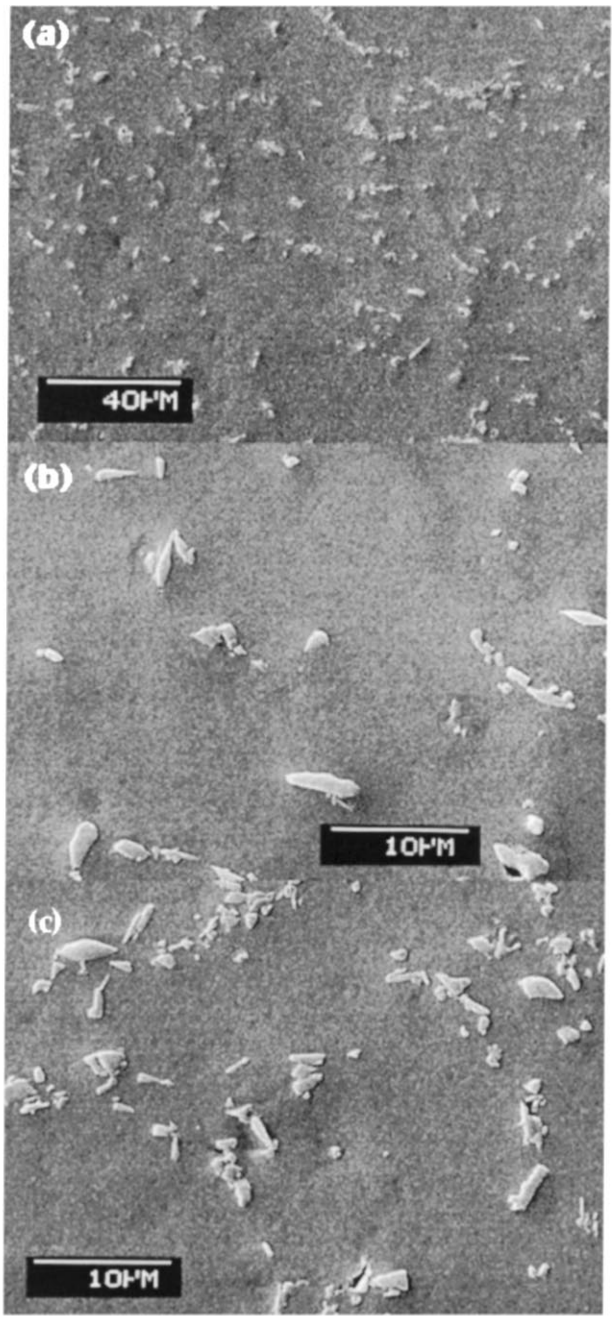

Figure 2 As-deposited distribution of SiC particles.

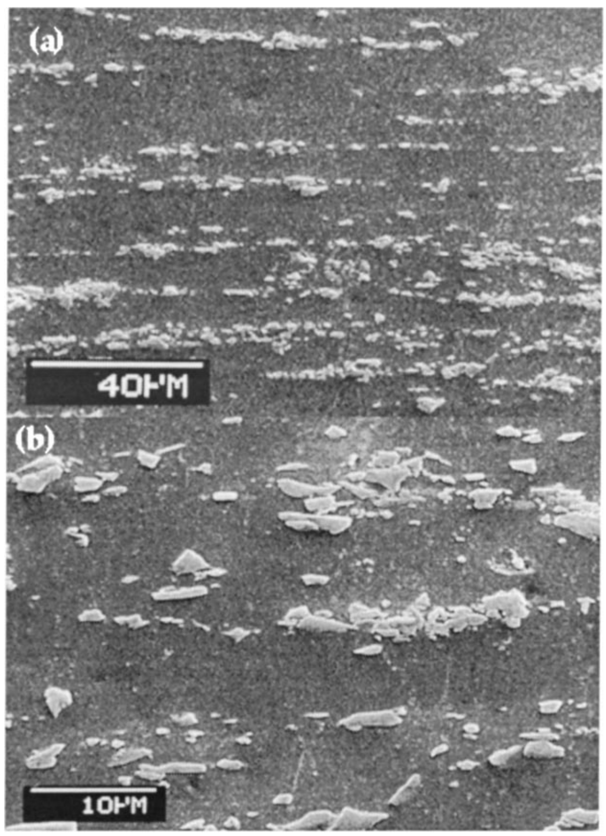

Figure 3 SiC particle distribution in longitudinal to extrusion direction.

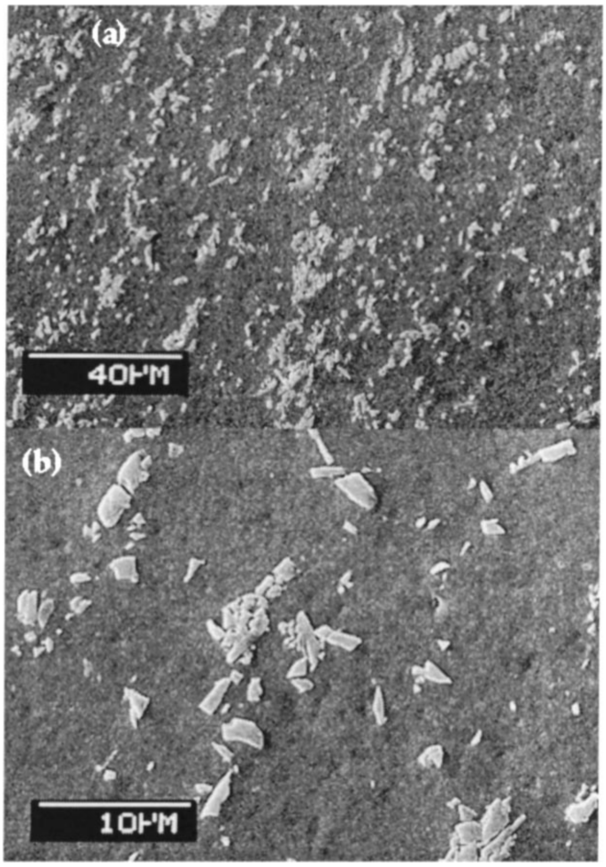

Figure 4 SiC particle distribution in perpendicular to extrusion direction.

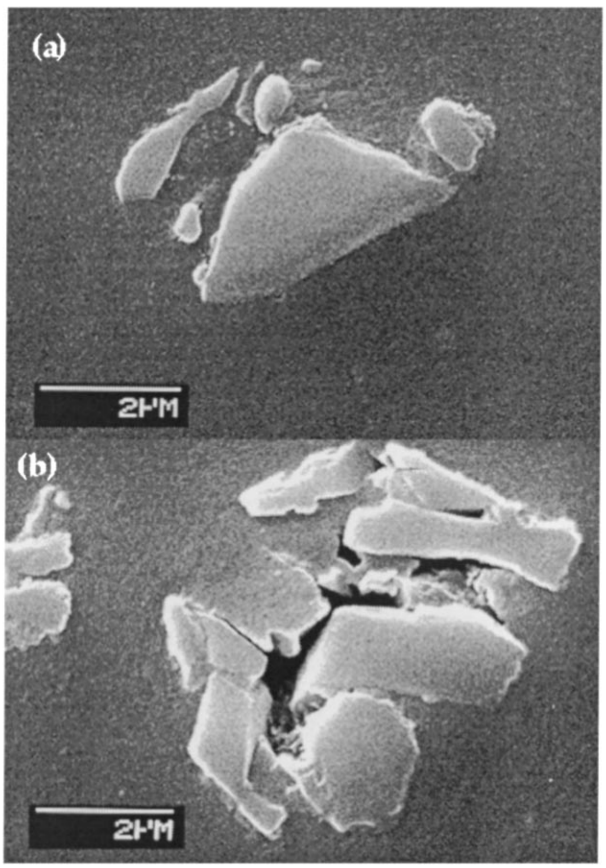

Figure 5 Two types of SiC particle agglomeration (as-deposited).

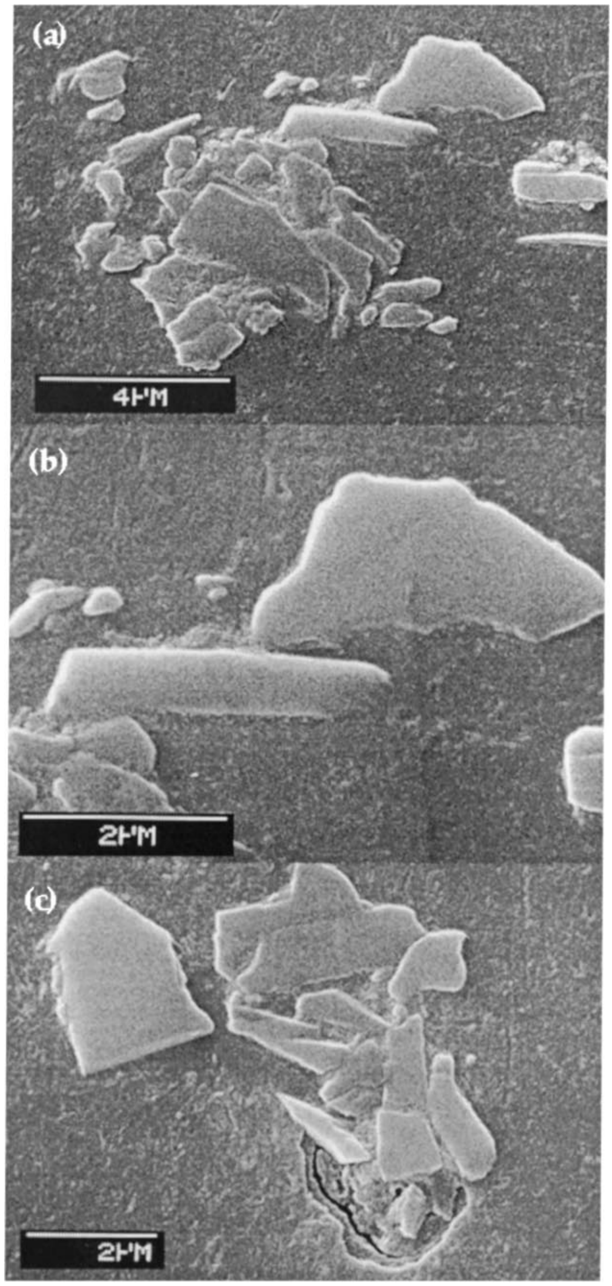

Figure 6 SiC particle agglomeration (as-extruded).

Two typical Al grain boundaries in as-deposited and as-extruded samples are shown in Fig. 11a and b, respectively. The boundaries are generally "clean" and free of participates. EDS analysis was carried out inside one grain and at the grain boundary. There is no indication of composition variation between the boundary and the inner grain.

4. Discussion

A homogeneous distribution of the reinforcing particles is an important factor in the superplastic forming of the spray formed MMCs. Typical thermomechanical processing is in general necessary to achieve the microstructural features required for the superplastic forming. Accomplishment of ultra-fine SiC particle injection into the metal sprays, in the present study therefore, would be challenging. This is due to that for fine particles, they have less mass momentum for injection

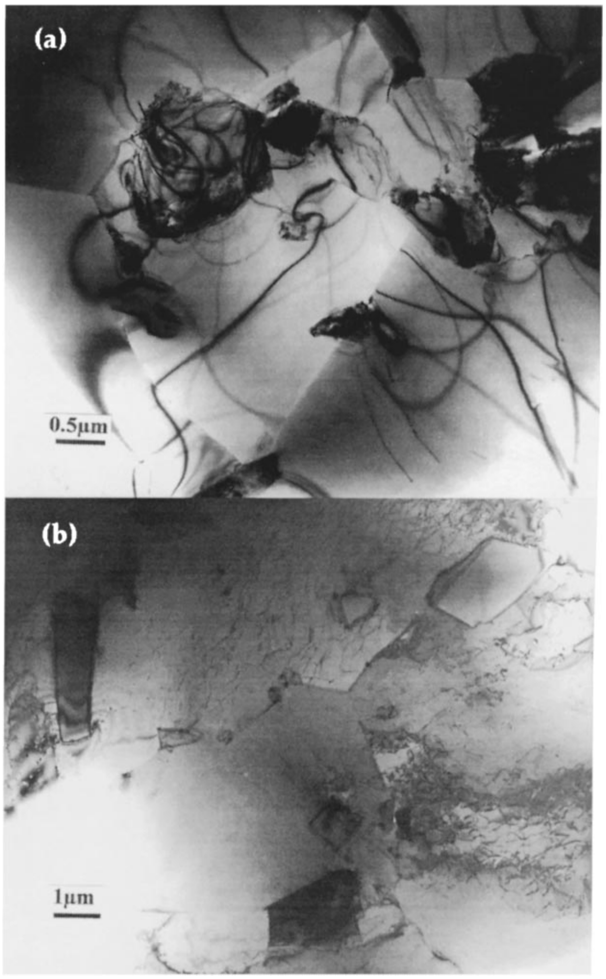

Figure 7 (a) TEM morphology of SiC particles in 5182 Al-Mg matrix (VF = 5.3%, as-deposited); (b) TEM morphology of SiC particles in 5182 Al-Mg matrix (VF = 5.3%, as-extruded).

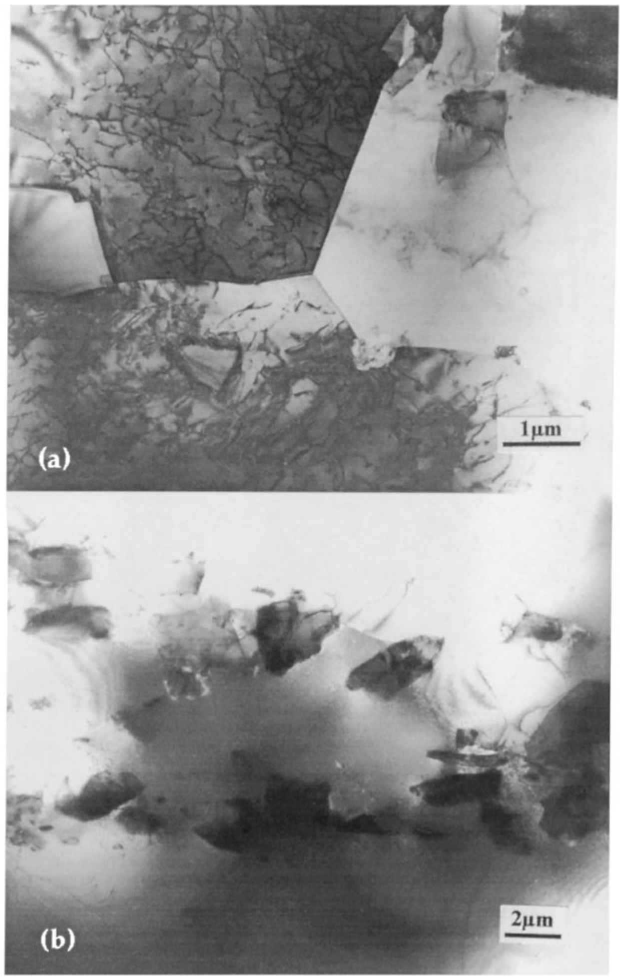

Figure 8 (a) TEM image indicating SiC distribution in 5182 Al-Mg matrix (VF = 5.3%, as-extruded, perpendicular to extrusion direction); (b) TEM image indicating alignment of SiC particles along extrusion direction (VF = 5.3%, as-extruded).

and are easy to agglomerate compared to large particles. In this section, preliminary results relating to above issues will be discussed, in particular addressing on the SiC particle distribution and effects of hot extrusion processing.

4.1. Particle distribution
It is documented [6] that in the spray forming processes, the reinforcing particle size distribution significantly influences the co-injection behavior, and therefore the final spatial distribution. For example, large reinforcing particles tend to exhibit a homogeneous distribution (less agglomeration), partly because they are easily fluidized and injected, partly due to their higher inertia. As a result, inspection of the scientific literature reveals that most published studies on spray forming of MMCs use reinforcing particles which are on the order of 10–20 μm [5, 7, 9, 26, 27]. From a mechanical behavior standpoint, it is well documented that there are benefits to be gained by co-injecting a distribution of particles in the 1 μm size range [13, 28–30]. These benefits include: grain refinement [28, 30], increased fracture resistance [29], and the possibility of superplasticity [13]. In view of the above discussion, the objective of this effort was to study the co-injection of fine particles during atomization. SiC particles with the median diameter of 1.2 μm and 2.0 μm, were used for the reinforcements.

Preliminary results, as shown in Fig. 2, indicate although it was possible to co-inject the fine particles, agglomeration of the SiC particles was still noted. Under the current research conditions, there are basically two types of agglomeration observed (Fig. 5). First one involves clusters SiC particles that retain connectivity with the matrix (Fig. 5a). Second one involves the presence of voids located inside of the SiC clusters (Fig. 5b). In general, particle clustering, and the resultant local heterogeneities are detrimental to the performance of particle reinforced MMCs. For example, particle clustering promotes void nucleation, growth, and coalescence [17]. It also initiates inhomogeneous plastic deformation resulting in low fracture toughness [23]. This phenomenon was evident in an experimental study of SiC particle reinforced Mg matrix composite which showed that cavities formed in regions of SiC agglomeration where the local stresses were high [24]. One approach that can be used to disperse the SiC particles is to extrude the as-deposited MMCs, which will be discussed in the following section.

4.2. Effects of thermomechanical processing
The influence of hot extrusion on the distribution of SiC particles was also examined, as shown in Figs 3 and 4. It can be seen that in the direction parallel to

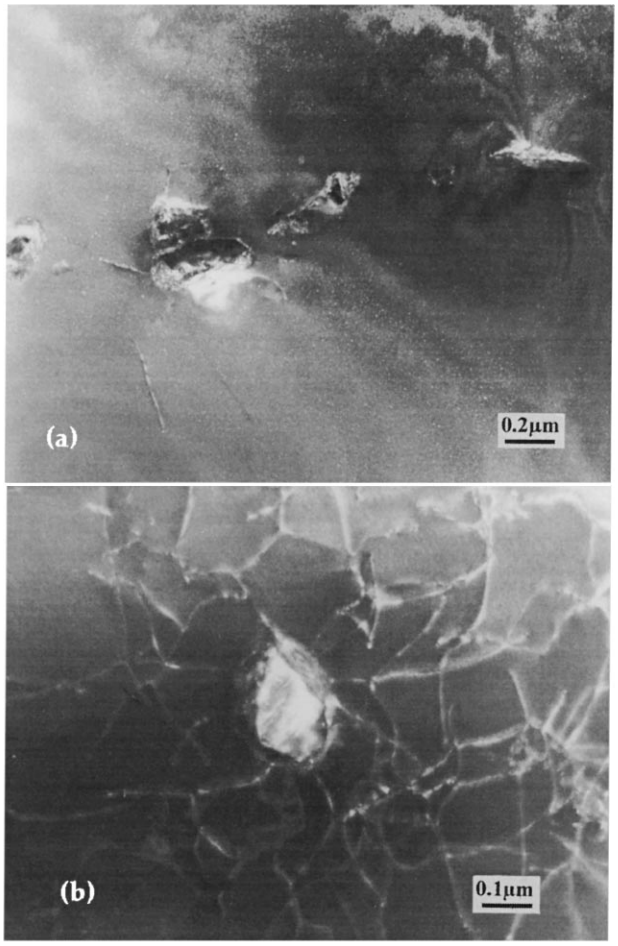

Figure 9 (a) Darkfield image showing formation of magnesium oxide in the vicinity of SiC particle (VF = 5.3%, as-extruded, parallel to extrusion direction); (b) Darkfield image showing formation of magnesium oxide in the vicinity of SiC particle (VF = 5.3%, as-extruded, perpendicular to extrusion direction).

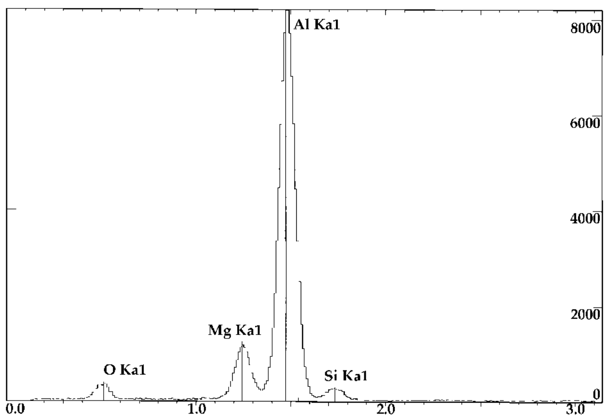

Figure 10 EDS spectra taken from the interface region showing high concentration of oxygen and magnesium.

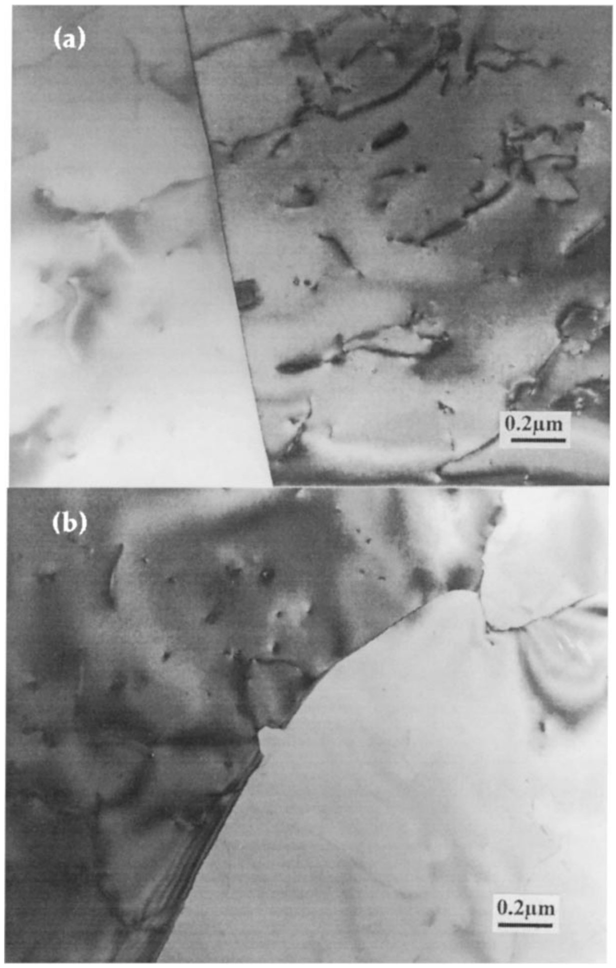

Figure 11 (a) Typical TEM image showing Al grain boundary (VF = 5.3%, as-deposited); (b) Typical TEM image showing Al grain boundary (VF = 5.3%, as-extruded).

the extrusion direction, banded distribution of SiC particles developed. This may be attributed to that: (1) extrusion processing resulted in the redistribution of SiC particles; and (2) original layered structure of SiC particles may, more or less, form during co-injection and deposition. In the cross-section perpendicular to extrusion direction however, SiC particles showed a relative uniform distribution. The banded structure of SiC particles was commonly formed after thermomechanical processing, such as hot extrusion, for conventional manufactured MMCs (I/M) [11]. In the I/M processing of MMCs, the reinforcing particles are pushed toward the grain boundary due to low solidification rate. Distribution of the reinforcing particles in the region of grain boundaries results in the formation of the banded structure when grains are deformed during thermomechanical processing. In the spray formed MMCs, the results show that SiC particles also exist along grain boundaries, as shown in Fig. 12. Comparing Fig. 12a and b demonstrates that the size of the reinforcing phase has insignificant influence in changing the particle distribution. It can be also seen in Fig. 12 that the grain size in the spray formed MMCs is much refined in the range of 20–50 μm, compared to that in the I/M MMCs which has been reported in the range of larger than 150 μm [16].

As described before, thermomechanical processing can modify the microstructure of the MMCs example, reduction of porosity and refine of grain size, and then improve the mechanical properties. For superplastic forming of the MMCs in particular, thermomechanical processing is generally needed to achieve the required fine grains. However, it is documented [11] that for conventionally manufactured MMCs some problems, fracture of large reinforcing particles and particle/matrix cohesion, are accompanied by thermomechanical processing. In the present research of the spray formed aluminum composite with very fine SiC

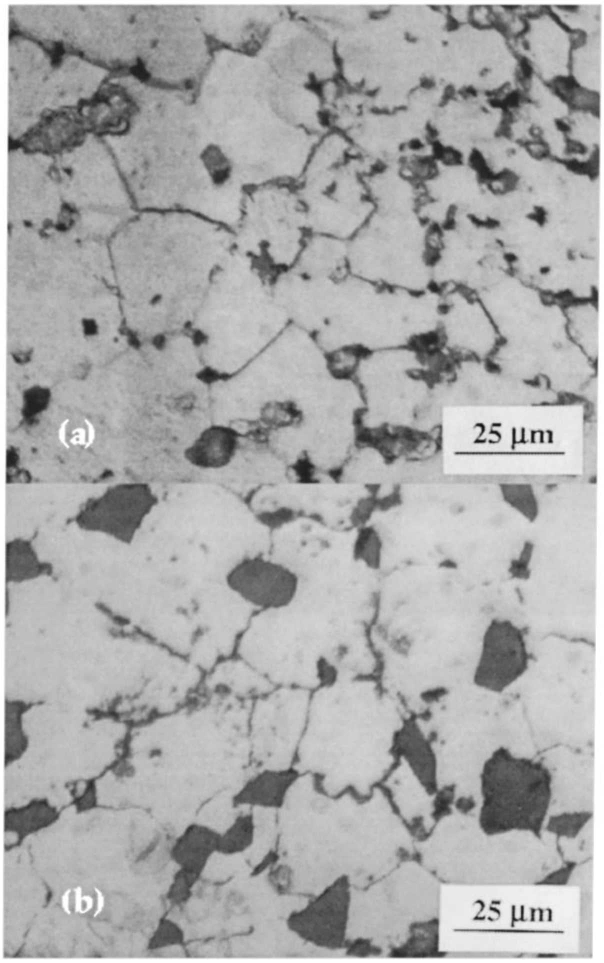

Figure 12 (a) SiC particle distribution in 5182 Al-Mg matrix (as-deposited), showing that most of SiC particles along grain boundary; (b) SiC particle distribution in Al-4.5Cu matrix (as-deposited), showing that SiC particles along grain boundary.

reinforcement, hot extrusion was conducted to investigate the effects of thermomechanical processing on the possibility of SiC fracture and SiC/matrix cohesion. As evidenced in Fig. 6a and b, extrusion processing did not show any effect on SiC fracture and SiC/matrix cohesion, even for the clustered SiC particles, the worst case. This suggests that cohesion between SiC and matrix is good and no reaction occurred during solidification, which can be supported by the clean interface also shown in Fig. 6b. As discussed previously, however, this interfacial reaction existed in the conventional fabrication of MMCs which were associated with slow solidification. In Fig. 6c, there exists a crack observed in the vicinity of SiC particles. Inspection of composition in the region reveals that it is a Mg-rich oxide which formed at the interface between SiC and Al matrix. Similar results of the oxide formation in the vicinity of SiC particles were also observed using TEM, as shown in Fig. 9. Therefore, care should be bore during melting of ingot alloy to avoid formation of oxides, which can help improve the mechanical properties of MMCs.

4.3. Microstructure characterization

An important characteristic of spray formed materials is the presence of a finite amount of non-interconnected pores [31, 32]. For strength and ductility critical applications, porosity should be reduced to the lowest possible value by optimizing the spray forming conditions or by thermal mechanical processing. The origin of porosity in spray formed materials may be attributed to one or a combination of the following mechanisms: (a) gas rejection, (b) solidification shrinkage, and (c) interparticle porosity. For MMCs however, there is an additional resource of porosity introduced by reinforcing particles. In the present study, this type of void most like forms during co-injection, which is due to the agglomeration (clustering) of very fine reinforcing particles without filling by liquid phase, as shown in Fig. 5b. The following thermomechanical processings, for example, extrusion and rolling, can not eliminate the voids, because the reinforcing particles (herein SiC) are rigid and difficult to be deformed. The existence of these voids is very detrimental to the mechanical properties of the spray formed materials and processing performance. Another phenomenon is higher dislocation densities in the region of matrix/SiC interface than in the matrix. Increased dislocation density in the vicinity of Al/SiC interface was resulted from (1) differential thermal expansion of Al and SiC during cooling [28] and (2) differential deformation behavior of Al matrix and SiC particles during hot extrusion.

5. Conclusions

1. SiC particles were dominantly in intergranular distribution the Al matrix. SiC particles tended to align along the extrusion direction in the as-extruded sample.

2. Two types of the particle agglomeration were observed. One is that SiC particles clustered with interconnection via Al matrix, and in this case, hot extrusion has insignificant promotion for the crack formation within the clustering. Another is that SiC agglomerated in accompany of the formation of voids inside, and hot extrusion does not help eliminate the voids.

3. Mg showed a tendency to segregate in the vicinity of SiC particles and forms oxide. The formation of the oxide promote initiating the crack in the region of oxide/SiC/matrix. However, there is no composition variation of Mg across Al grain boundaries.

4. There was no evidence that interfacial reaction between Al matrix and SiC occurred, which was superior to conventional processing of MMCs associated with interfacial reaction.

Acknowledgements

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