Phase Evolution - Property Relationships of PIMed 5 - 40 Vol.% SiCp - Reinforced Aluminium Composite

Tapany Patcharawit¹, Arada Ngeekoh¹, and Nutthita Chuankrerkkul²

¹School of Metallurgical Engineering, Suranaree University of Technology, 111 University Avenue, Suranaree Subdistrict, Meung, Nakhon Ratchasima, 30000, Thailand
²The Metallurgy and Materials Science Research Institute, Chulalongkorn University, Phayatai Rd., Pathumwan, Bangkok, 10330, Thailand

Abstract. Microstructure-mechanical property relationships of powder injection molded aluminium composite reinforced with 5 - 40 vol.% silicon carbide particulate (SiCp) has been investigated via thermal and phase analyses along with density and hardness testing. The samples were injection molded and sintered at 645 - 800 °C in N₂ atmosphere. Thermal analysis showed endothermic reactions around 632 - 643 °C, related to liquid phase formation. Exothermic reactions about 458 - 461 °C and weight gains around 471 - 479 °C were plausibly associated with AlN formation, which facilitated liquid phase sintering. The composite microstructure exhibited close interfaces between SiCp - Al and Al - Al for 5 - 20 vol.% SiCp addition. Higher SiCp addition however led to SiCp clustering, creating large pores and unreacted SiCp - SiCp interface, which prohibited both liquid flow and rearrangement of the solid grains and pore filling during liquid phase sintering. Optimum SiCp addition was achieved at 15 vol.%, giving the maximum bulk density at 2.68 g.cm⁻³ or at 94.2 % theoretical density. The maximum macro Vickers hardness values at 138.9 and 166.6 Hv were obtained in the as - sintered and age - hardened conditions respectively.

Keywords: thermal analysis; phase evolution; aluminium composite; powder injection molding, properties

1. Introduction
Composite materials have been of great interest for recent years for many engineering applications such as electrical, biomedical and automotive. Fabrication techniques in either solid, semi-solid or liquid routes yield different interfaces among the reinforcements and the matrices, which finally determine the composite properties. Powder injection molding or PIM is recognized as low cost and mass productive for complicate-small components. The use of PIM for composite fabrication has gained attention due to feasibility in powder formulation and process parameters [1-4]. However to achieve optimum properties, care has to be taken into account along the course of feedstock preparation, injection molding, debinding and sintering. In liquid phase sintering full densification is desirable, where situations such as wetting of liquid on solid grains and solubility of solid in liquid are required [5]. This research investigated phase evolution during liquid phase sintering of 5 - 40 vol.%
2. Experimental procedure

The aluminium composite of varying SiC\textsubscript{p} contents at 5, 10, 15, 20, 30 and 40 vol.\% was fabricated by powder injection molding using 73 μm Al - Cu powder of 4.77 wt.% Cu, 1.11 wt.% Mg, 1.01 wt.% Si, 0.12 wt.% Fe composition and SiC\textsubscript{p} of 20 μm size. Feedstocks prepared at 55% solid loading were subjected to Simultaneous Thermal Analysis (STA) using a NETZSCH STA 449 F3 Jupiter operating at a 40 K/min heating rate up to 900 °C in a N\textsubscript{2} feeding at 50 ml/min for the determination of liquid phase formation. Injection molding was operated at 170 °C to produce green samples. After solvent debinding, sintering was carried out at 645 - 800 °C using a 1 L/min N\textsubscript{2} flow rate. The sintered samples were subjected to age-hardening at 150 °C/6 h. Phase analysis was carried out using a JEOL - JSM 6061LV SEM + EDS and a D8 XRD analyzer.

3. Results

3.1. Simultaneous thermal analysis

STA result including Differential Scanning Calorimetry (DSC) and Thermogravimetric (TG) of feedstock prepared at 40 vol.% SiC\textsubscript{p} addition is demonstrated in Fig. 1, while Figs. 2 a) and b) demonstrate the onsets of endo/exothermic reactions (DSC1 - DSC5) and the onsets of weight loss (TG1 - TG5). Over the investigated temperature range up to 900 °C, thermal reactions and mass losses help to preliminarily determine suitable PIM and liquid phase sintering parameters, which are; i) the molding temperature, ii) the disposal of the multi-component binder and iii) the onset of liquid phase sintering for each formulation of the feedstock as follows:

![Figure 1. DSC and TG analyses of 40 vol.% SiC\textsubscript{p} feedstock up to 900 °C in N\textsubscript{2} atmosphere.](image)
Secondly, the TG graph reveals the onset of a small mass loss at 84.5 °C (TG1) due to vaporization of adsorbed water. Then significant mass losses at 263.7 °C and finished at 472.4 °C (TG2 - TG3), agreed with the vaporization of the binders. Therefore, soaking at 500 °C/0.5 h. was to assure the final disposal of the skeleton binder before reaching liquid phase sintering.

Thirdly as the temperature raised, endothermic reactions around 632 - 643 °C (DSC6), suggests the liquid phase formation. However, the actual sintering temperature had to raise up to 645 °C to 660 °C for aluminium composite reinforced with 5 - 20 vol.% SiCp addition in order to get effective sintering. In the case of 30 - 40 vol.% SiCp addition, the sintering temperature was 780 - 800 °C, in which refractoriness and agglomeration of the SiCp became prevalent. This will be later discussed.

3.2. XRD analysis

Comparative XRD results of as - sintered and age - hardened samples are shown in Figs. 3 a) and b) respectively for 40 vol.% SiCp reinforced aluminium composite. Both conditions share similar XRD peaks comprising the main spectra for Al and SiC as the matrix and reinforcement. AlN spectra were observed as the result of N2 sintering gas. Small spectra of Al2Cu and Mg2Si were detected according to the aluminium alloy powder composition.

![Figure 2](image_url)

*Figure 2.* Onset temperatures corresponding to a) thermal reactions and b) weight losses of feedstocks at varying SiCp additions.
**Figure 3.** XRD results of 40 vol.% SiC<sub>p</sub> reinforced aluminium composite in as-sintered (top) and age-hardened (bottom) conditions.

3.3. **SEM and EDS analysis**

Microstructures of aluminium, SiC<sub>p</sub> and feedstock are illustrated in Figs. 4 a) - d). It is noticed that the aluminium powder surface has become rougher after injection molding. It is possibly that the abrasive nature of angular shaped SiC<sub>p</sub> has scratched on the aluminium powder surfaces during feedstock preparation via ball-mill mixing, feedstock preparation, and powder injection molding. The disrupted oxide surface has later shown to facilitate magnesium migration and aluminium oxide consumption, favourable for liquid phase sintering. Discussion will be later introduced in this regard. In addition, poor particle packing is obtained at high SiC<sub>p</sub> content (30 - 40 vol.%) due to high surface energy of SiC<sub>p</sub>, leading to SiC<sub>p</sub> clustering along with large inter-particle porosity as shown in Figs. 5 e) and f), which is difficult to be rid of, even after liquid phase sintering. Macroscopic pores were found along large SiC<sub>p</sub> clusters at high SiC<sub>p</sub> content.
Figure 4. Powder morphology of a) aluminium alloy powder cross-sections, b) aluminium alloy powder and SiC\textsubscript{p}, c) feedstock and d) microstructure of feedstock at 10 vol.% SiC\textsubscript{p} addition.

Figure 5. Optical micrographs of 5-40 vol.% SiC\textsubscript{p} reinforced aluminium composite.

Figure 6. SEM micrographs of age - hardened SiC\textsubscript{p} - aluminium composite a) in as secondary electron mode, b) at higher magnification and c) in back - scattered electron mode.

SEM investigation reveals uniform distribution of SiC\textsubscript{p} and good interfaces between SiC\textsubscript{p} - Al and Al - Al for the composite containing low SiC\textsubscript{p} additions of 5 - 15 vol.%, as shown in Figs. 6 a) - c). Back scattered electron image displays contrast among SiC\textsubscript{p} (dark), aluminium alloy matrix (grey) and eutectic phase (bright). Such interfaces among these phases confirms liquid-phase sintering taking place. Fine precipitates can be differentiated from the aluminium matrix. EDS point analysis confirms compositions of aluminium matrix (spectrum 1), eutectic phase (spectrum 2), SiC\textsubscript{p} (spectrum 3) and...
precipitate phase of possibly $\text{Al}_2\text{Cu}$ (spectrum 4), as shown in Figs. 7 a) - e) for 40 vol.% SiC$_p$ reinforced aluminium composite in the age-hardened condition.

![Image](image-url)

**Figure 7.** EDS point analysis of 40 vol.% SiC$_p$-reinforced aluminium composite after age hardening.

![Image](image-url)

**Figure 8.** Measured and theoretical density of 5 - 40 vol.% SiC$_p$ reinforced aluminium composite.

### 3.4. Green and sintered density

Green and sintered density of the feedstocks and composite after liquid phase sintering is illustrated in Fig. 8. A slight increasing trend of the feedstocks’ green density is owning to SiC$_p$ addition. According to the rule of mixture and by taking the feedstocks prepared at 55% solid loading, density of aluminium alloy ($\rho_{\text{Al}} = 2.78$ g.cm$^{-3}$), density of SiC$_p$ ($\rho_{\text{SiC}} = 3.20$ g.cm$^{-3}$) and density of multi-component binder ($\rho_{\text{Binder}} = 0.94$ g.cm$^{-3}$), the theoretical green density of the feedstocks is found in a range of 1.95 - 2.02 g.cm$^{-3}$ for 5 - 40 vol.% SiC$_p$ additions respectively. The measured green density of the feedstock is 1.80-1.89 g.cm$^{-3}$ for 5 - 40 vol.% SiC$_p$ additions. Inter-particle porosity especially along SiC$_p$ clusters might have been the reason, which accounts for 91.9 - 93.6% theoretical density.
In contrast to green density reported earlier, the sintered density of the composite shows the optimum values at 2.68 g.cm\(^{-3}\) for the composite reinforced with 15 vol.% SiC\(_p\) addition. This accounts for 94.2% theoretical sintered density at the optimum value. Beyond this range, an adversative role of inter-particle porosity along the SiC\(_p\) clusters has interfered, as shown previously. The minimum values of 65.1% theoretical sintered density is for composite reinforced with 40 vol.% SiC\(_p\) addition. A significant reduction in sintered density at high SiC\(_p\) addition is due to poor particle-packing among Al - Al powders, Al powder - SiC\(_p\) and SiC\(_p\) - SiC\(_p\), which will be later discussed.

3.5. Macro vickers hardness
Aluminium composite of 5 - 40 vol.% SiC\(_p\) additions in the as-sintered and age-hardened conditions exhibits a similar trend on hardness result to that of sintered density, giving the maximum Vickers hardness at 138.9 H\(_v\) and 166.6 H\(_v\) for 15 vol.% SiC\(_p\) addition in the as-sintered and age-hardened conditions respectively, as shown in Fig. 9. It is believed that particle-packing among aluminium and SiC\(_p\) played a similar role to that of sintered density, but in a lesser extent due partly to greater hardness of SiC\(_p\) resisting the hardness indentation.

Figure 9. Macro Vickers hardness of 5 - 40 vol.% SiC\(_p\) reinforced aluminium composites.

4. Discussion

4.1. Phase evolution during liquid phase sintering
Aluminium composite has shown to experience liquid phase sintering, indicated by close Al - SiC\(_p\) and Al - Al interfaces especially for 5 - 20 vol.% SiC\(_p\) additions. The penetration of the aluminium along grain boundaries (less spherical grains) signifies good wettability between two adjacent interfaces [5]. The composite having 30 - 40 vol.% SiC\(_p\) addition however possessed very poor interfaces due to SiC\(_p\) clustering. Discussion on phase evolution during liquid phase sintering is now on i) major phase evolution during liquid phase sintering and ii) AlN formation.

First, phase evolution as evidenced from XRD, SEM and EDS analyses confirmed the Al - Cu alloy remained as the matrix with smaller SiC\(_p\) distributed throughout. A greater degree of SiC\(_p\) clustering was obtained at higher SiC\(_p\) addition. According to Al - Cu equilibrium phase diagram, the composite containing 4.77 wt.% Cu will experience the first formation of the liquid phase around 570 °C, and increasing liquid amount is expected towards 650 °C in the semi-solid regime. The DSC results also indicated the same range according to the endothermic reactions. Since the aluminium alloy - SiC\(_p\) composite is nonetheless considered as a non-equilibrium system and research by S. Wu, et. al., suggested the addition of SiC\(_p\) reinforcement increased both liquidus temperature (T\(_L\)) and eutectic temperature (T\(_E\)), depending on the amount of reinforcement [6]. In this research work, though the sintering temperature of 645 - 660 °C is exceeding that suggested from the Al - Cu equilibrium phase diagram, the solid - liquid range might be presumed according to the non-equilibrium system. As the
higher temperature proceeds, higher content of the liquid phase promotes greater diffusion favorable for grain rearrangement; hence, better particle - packing, especially for the composite possessing low SiCₚ content of 5 - 20 vol.%. It is explained that as the aluminium liquid melt spread on the SiCₚ surface, the sintered bond was dissolved, and the inter - particle pores, if smaller than that of the matrix grains, would be annihilated due to the capillary force to pull the solid grains together [5]. In addition to those aluminium matrix and reinforcement, minor phases such as Al₃Cu and Mg₃Si are recognized, confirmed by XRD and SEM + EDS analyses, both in the as - sintered and age - hardened conditions. Much finer precipitates after age - hardening therefore reveal less visible XRD spectra as illustrated in Fig. 4 b).

Secondly, though AlN are not the major phase (neither matrix nor the reinforcement), AlN spectra are however obvious from the XRD result. Since AlN is considered as a significant phase in promoting densification [7] and mechanical properties, discussion is then given herein. Evidence of exothermic reactions taking place at 458 - 461 °C (DSC4), corresponding to the weight gains on the TG curves at 471 - 479 °C (TG4) might possibly be related to the AlN formation. Several research indicated the possibility of AlN formation at temperatures as low as 530 - 540 °C [8, 9], by direct nitridation or self - nitridation. It was explained that the Al₂O₃ layer on the aluminium powder was reduced by magnesium [10]. The Al₂O₃ layer was then consumed to disclose the aluminium, which is readily reacted with the N₂ within the sintering atmosphere to finally obtain AlN. The possible reactions proposed are as follows [7, 10]

\[ 3\text{Mg} + \text{Al}_2\text{O}_3 \rightarrow 3\text{MgO} + 2\text{Al} \]  

or

\[ 3\text{Mg} + 4\text{Al}_2\text{O}_3 \rightarrow 3\text{MgAl}_2\text{O}_4 + 2\text{Al} \]  

\[ 2\text{Al} + \text{N}_2 \rightarrow 2\text{AlN} \]

Alternatively, research by S.-H. Kim, et. al, proposed two steps of nitridation: i) the nitridation of aluminium via the native oxide layer in eqs. 4 - 5) and ii) direct nitridation of aluminium melt [11].

\[ \text{Al}_2\text{O}_3 (s) + \text{N}_2 (g) \rightarrow \text{1AlION} (s) + \frac{1}{2} \text{O}_2 (g) \]  

\[ x\text{Al}_2\text{O}_3 (s) + \text{Al} (l) \rightarrow y\text{AlN} (s) + \text{O}_2 (g) \]

Their research suggested the nitridation around 620 °C where the weight gain and exothermic reaction were detected. T. Okada, et. al, [8] on the other hand, suggested the temperature as low as 520 °C is for partial nitridation and where complete direct nitridation was obtained at 540 °C, depending on the compact pressure employed. However, P. Sthapitanonda and J. L. Margrave [12] suggested the initial nitridation at 475 °C detected by weight gain at 0.10 µg/cm². In this research, the nitridation temperature is recognized by the weight gain around 472 °C. It is proposed here that with the addition of hard/abrasive SiCₚ, such Al₂O₃ layer might have been disrupted during ball-mill mixing and PIM process [13]. This in turn offers a fast track for Mg to migrate through such oxide layer to reduce the Al₂O₃ film at low temperature as low as 300 - 500 °C [14].

Thirdly, if reactions towards the liquid phase is now considered, the weight gains detected on TG curves (TG5), showing the onsets at 643.7 and 847 °C for the feedstocks having 10 and 40 vol.% SiCₚ addition for comparison. Though it is known that SiC is readily attacked by the molten aluminium to give AlₓCₙ [15] via dissolution and precipitation in 657 - 827 °C temperature range (eq. 6), no AlₓCₙ was detected by XRD results in this research. This is owing to peroxidation of SiCₚ at 1000 °C/4 h prior to feedstock preparation to give the protective covering SiO₂ film (eq. 7) against the AlₓCₙ formation during liquid phase sintering [16, 17].

\[ 4\text{Al} (l) + 3\text{SiC} (s) \rightarrow \text{Al}_2\text{C}_3 (s) + \text{Si} (s) \]  

\[ 2\text{SiC} (s) + 3\text{O}_2 (g) \rightarrow 2\text{SiO}_2 (g) + 2\text{CO} (g) \]
Such SiO₂ film can be attacked by aluminium melt to form elemental silicon via redox reaction, which later diffuses to the aluminium melt whereas aluminium will diffuse in the counter direction towards SiO₂, giving the Al₂O₃ formation (eq. 8) as proposed by M. Yan and Z. Fan [18]. Evidence of free Si and Al₂O₃ was also detected via XRD result.

\[ 4\text{Al} (l) + 3\text{SiO}_2 (s) \rightarrow 3\text{Si} (l) + 2\text{Al}_2\text{O}_3 (s) \]  

(8)

In summary, liquid phase sintering of SiCₚ - aluminium composite involved multiple solid phases, which have different solubility-temperature-relations. Phase evolution during liquid phase sintering of PIMed SiCₚ - reinforced aluminium composite is then proposed as depicted in Fig. 10 (adopted from Randall M. German [5]). First, i) solid state sintering via Al₂O₃ surface film reduction by magnesium before entering the liquid phase sintering. As preferential dissolution of solids by the liquid melt during heating is at the grain boundaries [19], it might be that after the aluminium melt protruded out from the disrupted Al₂O₃ surface film, AlN formation then progressed as aluminium melt content increased with increasing temperature. In the presence of magnesium, wettability was enhanced and promoted ii) liquid flow and rearrangement of the solid grains. Then iii) solution - reprecipitation took place plausibly by the aluminium melt, acting as the transient liquid, to dissolve smaller aluminium solid grains and reprecipitated in the tension area of larger grains. Aluminium melt attack on SiO₂ film might also be recognized along with continuous AlN formation during this stage before proceeding to the final densification by iv) solid phase sintering. Densification of the composite was thus enhanced along the course of liquid phase sintering.

![Schematic of microstructure evolution in liquid phase sintering of PIMed SiCₚ - reinforced aluminium composite.](image)

**Figure 10.** Schematic of microstructure evolution in liquid phase sintering of PIMed SiCₚ - reinforced aluminium composite.

4.2. Effects of SiCₚ addition on properties of PIMed aluminium composite

Increasing SiCₚ content to 30 - 40 vol.% increased the solid fraction that required greater heat mass due to SiCₚ’s refractoriness. High surface energy and angular shape of SiCₚ resulted in clustering which increased unreacted SiCₚ - SiCₚ interface. This poor interface cannot be wet by aluminium melt during liquid phase sintering, leading to excessively large pores. If pores are larger than the grain size, in the case of the composite having high SiCₚ content of 30 - 40 vol.%, they are difficult to be filled by
the liquid melt and required considerable time. Unfortunately, if there is any gas trapped in the pores, such as O$_2$ generating during AlN formation, then the combined effects of gas pockets in the pores made them spherical and difficult to collapse, which prohibited the final densification. This led to reduced density and hardness of the composite at higher SiC$_p$ addition of 30 - 40 vol.%. If pores are smaller than the solid particles (Al powder and SiC$_p$), they will be later filled with the liquid aluminium due to the capillary force. Shrinkage then resulted and this is the case for the composite having 5 - 20 vol.% SiC$_p$ addition, where volumetric shrinkage was reported to be 35 - 40% [20].

5. Conclusions
1) The PIMed 5 - 40 vol.% SiC$_p$ reinforced aluminium composite experienced liquid phase sintering over the investigated sintering temperatures, suggested by thermal analysis.
2) Aluminium composite at 5 - 20 vol.% SiC$_p$ addition exhibited close Al - Al and Al - SiC$_p$ interfaces indicating liquid flow and rearrangement of the solid grains, leading to densification and shrinkage. However, high SiC$_p$ addition at 30 - 40 vol.% resulted in large pores along SiC$_p$ clustering, prohibited pore filing and wetting.
3) The optimum SiC$_p$ addition is 15 vol.% to offer the maximum bulk density at 2.68 g.cm$^{-3}$ at 94.2 % theoretical density and the maximum macro Vickers hardness at 138.9 and 166.6 H, in the as - sintered and age - hardened respectively.
4) AlN was detected during liquid phase sintering, which improved densification and hardness.

References
[1] H. Abdoos, H. Khorsand, and A.A. Yousefi: Int. J. Mater. Res. Vol. 108 (2017) p. 237-244.
[2] H. Ye, X.Y. Liu, and H. Hong: J. Mater. Process Tech. Vol. 200 (2008) p. 12-24.
[3] V. G. Dhore, W.S. Rathod, and K.N. Patil: Mater. Today Proc. Vol. 5 (2018) p. 20690-20698.
[4] S. G. Lamarre, V. Demers, and J.-F. Chatelain: Int. J. Adv. Manuf. Tech. Vol. 91 (2017) p. 2595–2605.
[5] R.M. German, in: Sintering: From empirical observations to scientific principles, Publications/Elsevier (2014) in press.
[6] S. Wu, P. An, Y. You, T. Kanno, and H. Nakae: in 13th International Conference on Composite Materials (ICCM13) (2001) Beijing, China.
[7] T. W. Kim, Mater. Sci. Eng., A: Vol. 483-484 (2008) p. 648-651.
[8] T. Okada, M. Toriyama, and S. Kanzaki: J. Mater. Sci. Vol. 35(2000) p. 3105-3111.
[9] G. B. Schaffer, and B.J. Hall, Metall. Mater. Trans. A. Vol. 33 (2002) p. 3279-3284.
[10] S. Zhongliang, G. Mingyuan, L. Junyou, L. Guoquan, L. Jae-chul, Z. Di, W. Renjie: Chin Sci Bull. Vol. 46 (2001) p. 1984-1952.
[11] S. H. Kim, J. H. Noh, J. P. Ahn, J.-C. Lee, H. Kwon, J. Lee, H. R. Yang, and K. B. Lee: Metall. Mater. Trans. A, Vol. 46 (2015) p. 496-504.
[12] P. Sthapitanonda and J. L. Margrave: J. Phys. Chem. Vol. 60 (1956) p. 1628-1633.
[13] M. P. Thomas, and J.E. King: J. Mater. Sci. Vol. 29 (1994) p. 5272-5278.
[14] A. Kimura, M. Shibata, M. Katayama, T. Kanie, and H. Takada: Appl. Phys. Lett. Vol. 70 (1997) p. 3615-3617.
[15] J. C. Viala, F. Bosselet, V. Laurent, and Y. Lepetitcorps: J. Mater. Sci., Vol. 28 (1993) p. 5301-5312.
[16] J. Roy, S. Chandra, S. Das, and S. Maitra: Rev. Adv. Mater. Sci. Vol. 38 (2014) p. 29-39.
[17] A. Ureña, E. E. Martínez, P. Rodrigo, and L. Gil: Compos. Sci. Technol. Vol. 64 (2004) p. 1843-1854.
[18] M. Yan, and Z. Fan: J. Mater. Sci. Vol. 63 (2001) p. 285-295.
[19] R. M. German, P. Suri, and S.J. Park: J. Mater. Sci. Vol. 44 (2009) p. 1-39.
[20] T. Patcharawit, A. Ngeekoh, U. Kitkhamthorn, and N. Chuankrekkul: in 2019 4th International Conference on Design (D2ME 2019) Phuket, Thailand.