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Enhanced tensile properties of aluminium matrix composites reinforced with graphene encapsulated SiC nanoparticles

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Abstract

Due to a high propensity of nano-particles to agglomerate, making aluminium matrix composites with a uniform dispersion of the nano-particles using liquid routes is an exceptionally difficult task. In this study, an innovative approach was utilised to prevent agglomeration of nano-particle by encapsulating SiC nano-particles using graphene sheets during ball milling. Subsequently, the milled mixture was incorporated into A356 molten alloy using non-contact ultrasonic vibration method. Two different shapes for graphene sheets were characterised using HRTEM, including onion-like shells encapsulating SiC particles and disk-shaped graphene nanosheets. This resulted in 45% and 84% improvement in yield strength and tensile ductility, respectively. The former was ascribed to the Orowan strengthening mechanism, while the latter is due primarily to the fiber pull-out mechanism, brought about by the alteration of the solidification mechanism from particle pushing to particle engulfment during solidification as a consequence of high thermal conductive graphene sheets encapsulating SiC particles.

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Abstract

Due to a high propensity of nano-particles to agglomerate, making aluminium matrix composites with

a uniform dispersion of the nano-particles using liquid routes is an exceptionally difficult task. In this

study, an innovative approach was utilised to prevent agglomeration of nano-particles by

encapsulating SiC nano-particles using graphene sheets during ball milling. Subsequently, the milled

mixture was incorporated into A356 molten alloy using non-contact ultrasonic vibration method. Two

different shapes for graphene sheets were characterised using HRTEM, including onion-like shells

encapsulating SiC particles and disk-shaped graphene nanosheets. This resulted in 45% and 84%

improvement in yield strength and tensile ductility, respectively. The former was ascribed to the

Orowan strengthening mechanism, while the latter is due primarily to the fiber pull-out mechanism,

brought about by the alteration of the solidification mechanism from particle pushing to particle

engulfment during solidification as a consequence of high thermal conductive graphene sheets

encapsulating SiC particles.

Keywords: Metal-matrix composites (MMCs) (A); Graphene sheets (A); Mechanical properties (B);

Casting (E)

1. Introduction

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1   The achievement of both strength and ductility for aluminium alloys reinforced with ceramic

2   particulates is very useful for a wide range of safety applications. However, although aluminium

3   alloys reinforced with ceramic particulates enhance the tensile strength, they suffer from inadequate

4   ductility [1, 2]. This is, in fact, a well-known bottleneck that limits the widespread engineering

5   application of micro-composites especially when there is high ceramic particle content [3, 4].

6   To attain a higher strength and retain ductility of the composite, nano-sized ceramic particles are often

7   used [5, 6]. The result is a metal matrix nano-composite (MMNC) [7, 8]. In such cases, it is extremely

8   challenging to distribute and disperse the nano-particles uniformly in the metal matrix. This is

9   especially true for using liquid based processing routes such as casting, because of the large surface to

10   volume ratio and the poor wettability of nano-particles in most metallic melts [9, 10]. It was found

11   that composites manufactured specifically by liquid methods such as stir casting suffer from particle

12   pushing [11], resulting in rejection and agglomeration of particles from the growing solid/liquid

13   interface during solidification. These problems easily induce the agglomeration and clustering of the

14   nano-particles in the matrix, prompting low tensile properties, especially ductility, associated with

15   intergranular fracture mode in the final solidified material [12-14].

16   The key to prolonged ductility is, therefore, to disperse these nano-particles into the grain interior,

17   rather than having them agglomerated and concentrated at the grain boundaries, which can endanger

18   elongation by causing cracks in nano-particles settled at the grain boundaries [13]. The former is

19   accomplished by manipulating the shape of the interface and its curvature, controlling the interaction

20   between the particle and the interface. It has also been suggested that the shape of the interface behind

21   the particle is also dependent on the thermal conductivity of the particle and the melt [15, 16]. Khan et

22   al. [16] showed that when the thermal conductivity of the particle is greater than that of the melt, the

23   shape of the interface behind the particle changes from convex to concave. This difference at interface

curvature brings about engulfment of particles in the matrix instead of segregation and pushing into

the interdendritic regions, conferring improved tensile properties on the produced composites [17].

3 Many researchers have focused on using innovative methods to incorporate nano-particles into the

4 molten aluminium, making an MMNC with a suitable dispersion and avoiding nano-particle

5 agglomeration [10]. The milling of nano-particles with metallic powders such as aluminium and

6 ultrasonic assisted casting methods, especially in the semi-solid state, are the most important methods

7 which have been proposed in this regard. However, these methods are still in development, especially

8 where a high reinforcement loading is sought [3, 14, 18] in the implementation of thermal models to

9 predict the interaction at the solid/liquid interface during solidification.

10 In addition to the unprecedented characteristic of graphene, i.e. a single-atom-thick sheet of sp^2

11 hybridised carbon atoms, as a strengthening nanofiller in the world of polymer matrix composites [19,

12 20], recent studies have shown that graphene can also be considered as an effective reinforcement for

13 metal matrices [21]. However, to the best of our knowledge, most of these studies [21, 22] have only

14 considered the mechanical property changes after the implantation of graphene nanosheets (GNSs) as

15 a new nano filler for metal matrix composites, but exploiting the promising characteristics of GNSs,

16 such as the high thermal conductivity and anchoring nano particles, to harness the structural

17 uniqueness and full potential of utilising nano-particles during the fabrication process remains largely

18 unexplored. For instance, it has been reported that graphene sheets possess the unique feature of

19 having a two-dimensional shell(s) which can nucleate and anchor nano-particles on the edges and

20 surface[23, 24], however, the ability of graphene sheets to alleviate the agglomeration of nano-

21 particles during solid and liquid processing for the production of meal matrix composites has hitherto

22 not been reported.

23 In this study, an innovative nanocapsulating route is implemented to exploit the high thermal

24 conductivity and flexibility of graphene sheets as wrapping shells to diminish the pushing and

1   agglomeration of SiC nano-particles during milling and the subsequent semi-solid casting process.

2   The effect of using 1 Wt. % GNSs to alleviate the agglomeration of nano SiC particles and subsequent

3   enhancement in tensile properties of the composite, produced using a process encompassing milling

4   and semi-solid stir casting, was investigated using high resolution transmission electron microscopy

5   (HRTEM) and tensile tests, respectively. In order to gain insight into the relationship between the

6   microstructure of the fabricated composite and its tensile properties , two mathematical models were

7   developed, making use of the Orowan strengthening mechanism, and the models were further

8   validated with tensile test results.

9   **2. Experimental Procedures**

10   In order to prepare a mixture containing nano SiC and GNSs reinforcements, high purity aluminium

11   powder (45 µm, supplied from Alpha Aesar Company with 99.5 % purity), a sufficient amount of

12   nano-β-SiC particles (45 nm, supplied from Nanostructured & Amorphous Materials, Inc.) and pure

13   pristine monolayer graphene with the average lateral size of 550 nm (supplied from Graphene

14   Supermarket) were used.

15   The ball milling process was performed in a Fritsch Pulverisette P5 planetary ball mill without

16   interruption under high purity (99.999%) argon gas in a liquid nitrogen environment (cryomilling).

17   During cryomilling, liquid nitrogen was constantly added to compensate for evaporation. The stainless

18   steel vial was sealed with an elastomeric O ring. The stainless steel balls to powder weight ratio is

19   15:1, and the rotation rate of the vial is 250 rpm under a total milling time of 2h. The amount of GNSs

20   and SiC nano-particles was adjusted to 83 Wt. % SiC and 17 Wt. % graphene. These components

21   were milled for 0.5h without aluminium powder. Subsequently, the milling was continued for 1.5h by

22   adding aluminium powder to the mixture, containing graphene and SiC, by setting the aluminium

23   weight equal to 45Wt. % of the total SiC and graphene powders, to enhance the incorporation of the

24   nano SiC particles into the molten aluminium.

1. Powder injection into molten A356 aluminium alloy was conducted with high purity (99.999%) argon

2. atmosphere (6 lit/min) in the semi-solid state. Table 1 demonstrates the chemical composition of the

3. A356 alloy used in this study. Two distinct methods including (a) as received SiC particles and (b)

4. composite powder containing aluminium powder and SiC particles encapsulated by graphene sheets

5. (prepared, as noted above, by the milling process) were utilised. After the entire alloy in the crucible

6. was melted, it was cooled to 605°C and held at this temperature. This temperature lies in the solid-

7. liquid range and corresponds to a solid fraction of about 0.30 [25].

8. Then, stirring of the semi-solid alloy (using a graphite impeller) at 400 rpm was initiated, while

9. prepared powders were added to the uniformly formed vortex over a time period of approximately 5

10. min associated with adding 1Wt.% Mg as a wetting agent. Simultaneously, non-contact ultrasonic

11. casting was utilised to apply vibration to the prepared melt. This was done using an ultrasonic

12. chamber (Bandelin-Germany Make – Model: RK – 100H), which can vibrate at a frequency of 35

13. kHz. After the completion of particle feeding, mixing was continued for an extra 1 min. Finally, the

14. composite slurry was poured into a pre-heated cast iron mould using a bottom-pouring system. The

15. composites fabricated using as-received SiC particles and composite powder are denoted herein as

16. AR-SiC and preform samples, respectively.

17. The density of the samples was measured by the Archimedes method in order to calculate the porosity

18. of the samples. In addition, in order to investigate the formation of GNSs in the matrix and around the

19. SiC particles in the composite, HRTEM was employed using a Philips CM200 at an accelerating

20. voltage of 200 kV. The morphology evolution of the powders during milling and the fracture

21. behaviour of the fabricated composites were characterised using Field Emission Scanning Electron

22. Microscopy (FE-SEM) performed in a HITACHI S4160.Tensile testing was carried out using a

23. Hounsfield universal test machine at a cross-head speed of 0.5 mms^{-1}. The dog-bone shaped tensile

1 specimens had a gauge size of 6 mm in diameter and 30 mm in length, according to ASTM: B557M-

2 10.

3. Results and Discussion

3.1. Morphological characterization of powders

5 Fig. 1(a) shows the morphology of Al-55 Wt. % SiC-12 Wt. % graphene powder (preform), set to

6 reach the final composition after casting. As shown in Fig. 1(a), the size of the agglomerated particles

7 after milling is smaller than 1µm, which can accommodate better dissolution and lower agglomeration

8 during subsequent semi-solid stir casting. Basically, the dissolution of finer milled powders in the

9 melt is easier than that of larger agglomerated ones. Three important phenomena are responsible for

10 formation of nanodispersions before solidification. First, the dissolution of aluminium powders during

11 injection of powders into the melt. In fact, aluminium powders act as a carrier for ceramic particles to

12 the melt and protect them from any contact with the surface of the melt and alumina layer, and after

13 their dissolution, the nanoparticles will be released in the matrix. Second, the power of ultrasonic

14 vibration causes the agglomerated particles not being sintered. In fact, it is envisaged that aluminium

15 powders which are in the inner part of an agglomerated nanoparticles act as a binder at 605 °C to

16 avoid particles separation and release, which only ultrasonic vibration could separate these

17 nanoparticles during stirring. Finally, the importance of using semi-solid stirring must be considered.

18 Indeed, a high amount of shear stress during mechanical blending in the semi-solid stirring causes the

19 agglomerated particles to easily separate from each other.

20 Fig. 1(b) demonstrates the high magnification image of the agglomerated particles in Fig. 1(a). As can

21 be seen in Fig. 1(b) and corresponding cross section as a right corner image, a uniform distribution of

22 SiC particles inside the aluminium matrix was achieved after the milling process, due to the formation

23 of graphene sheets around SiC particles in the first step of milling. In fact, it is believed that the

formation of graphene sheets can be a good strategy to diminish the high propensity of nano-particles

for agglomeration during the milling process.

HRTEM experiments have been utilised to reveal the formation and dispersion of graphene sheets

around SiC particles and inside the preform sample. Fig. 2(a) demonstrates the representative HRTEM

image of graphene sheets encapsulating SiC particles during the milling process, appearing in the

form of onion-like shells around the SiC particles. It can be seen that this innovative process has a

unique capability to encapsulate SiC particles with bilayer or trilayer graphene sheets bent around the

SiC particles.

As shown in Fig. 2(a), the outer graphene shells (white arrow) tightly surrounded SiC particles

without any gap, following the surface curvature of the ceramic particles in order to minimise surface

energy of system including particles and graphene shells. Basically, the impact forces produced during

the initial step of milling is what bends the sp^2 around the SiC particles, thus forming these onion-like

shells.

Fig. 2(b) demonstrates the TEM image of SiC particle distribution in the composite powder. As can be

seen, a uniform distribution of SiC particles is achieved. In fact, besides the unique characteristic of

this process for producing a bilayer or trilayer graphene shell encapsulating the SiC particles (Fig. 2

(a)), this process is also able to prevent the agglomeration of nano SiC particles in the milled powder,

as shown in Fig. 2(b), substantiating the results shown in Fig. 1(b). As shown in Fig. 2(c), the TEM

elemental x-ray map also authenticates the formation of well-dispersed SiC particles throughout the

composite powder.

3.2. Composite structure

3.2.1. FE-SEM investigations

Fig. 3 represents the FE-SEM microstructure of the AR-SiC (Fig. 3(a)) and preform (Fig. 3(b))

samples, respectively. There are four important points that can be deduced from Fig. 3. First, the

formation of agglomerated SiC nanoparticles is observed in the AR-SiC sample (Fig. 3(a)) compared

with a uniform distribution of these particles in the preform sample (Fig. 3(b)), despite the fact that

some clusters remain in the matrix (black arrows in Fig. 3(b)). As shown in Fig. 3(a) by black arrows,

SiC nanoparticles in the AR-SiC sample have this propensity to be agglomerated within aluminium

matrix associated with formation of microvoids at the interface of these particles and surrounding

matrix, resulting in lower tensile properties.

Second, the remain of nano-gaseous pores after stirring seems to be inevitable during the semi-solid

state process for both samples due to a high viscosity of the melt, even when ultrasonic waves were

used. Third, the amount of nanoparticles is considerably higher for preform sample containing

graphene nanosheets and aluminium powders. Forth, the presence of air gap in the agglomerated

ceramic particles and formation of solidification shrinkages around these agglomerated particles could

be seen in Fig. 3a. There is also some evidence of formation of nano pores within the matrix.

3.2.2. TEM investigations

In Section 3.2.1, nanostructures of the produced composites were characterised using TEM, associated

with schematic illustrations to give a better insight into the effect of graphene sheets on the

nanostructures of the samples. Additionally, the effect of graphene sheets on manipulation of

solidification behaviour of the samples, playing an important role in manifestation of the

aforementioned nanostructures, is investigated in Section 3.2.3.

Fig. 4 represents TEM nanostructure images of AR-SiC (Fig. 4(a, b)) and preform samples (Fig. 4(c-

f)) after semi-solid stir casting. Fig. 4(b), (d) and (f) are schematic illustrations corresponding to the

nanostructures seen in Fig. 4(a), (c) and (e), respectively. As shown in Fig. 4(a), nano SiC particles in

the AR-SiC sample have a high tendency to agglomerate during stir casting in order to reduce their

free surface energy. As can be seen in Fig.4 (a), the vast majority of SiC particles in the AR-SiC

sample have a high propensity to agglomerate at grain boundaries instead of within the grain interior,

1 and this is attributed to the effect of the particle pushing mechanism during solidification, as shown by

2 arrows in Fig. 4(b). However, as can be seen in Fig. 4(c), in the case of preform samples, the majority

3 of well-dispersed SiC particles reside in the grain interior rather than at the grain boundaries, and this

4 is ascribed to the effect of the particle engulfment mechanism during solidification, as demonstrated

5 by arrows in Fig. 4(d).

6 In fact, the better distribution of SiC particles especially in the grain interior of the preform sample

7 compared to the formation of agglomerated SiC particles at the grain boundaries of the AR-SiC

8 sample can be related to various parameters involving manufacturing processes (e.g. ball milling and

9 semi-solid routes) and other mechanisms controlling the solidification process after semi-solid

10 casting.

11 First, regarding the role of milling, it is believed that graphene shells wrapping nano SiC particles can

12 be in charge of the uniform dispersion of these particles in the milled composite powder, as shown in

13 Fig. 2(c). From an energetic standpoint, the quasi-spherical carbon and onions are the most stable

14 form of carbon particles [26]. When the highly curved graphene sheets are obtained as a result of high

15 flexibility of graphene sheets and impact forces applied during ball milling, they are in a metastable

16 state in the light of the theory of minimisation of surface area, so the need to minimise the energy

17 drives this curling up to spherical forms like onions. Under this circumstance, nano SiC particles can

18 be a favourable substrate to be wrapped by highly curved graphene sheets which in turn diminishes

19 the total energy of system by alleviating the agglomeration of nano SiC particles.

20 Second, semi-solid processing also plays an important role in the uniform distribution of the SiC

21 particles in the preform sample. In fact, it is believed that creation of a vortex in the semi-solid stirring

22 process breaks solid dendrites at 605 $^{\circ}$C because of higher friction between the SiC particles and the

23 aluminium alloy matrix. This further induces a homogeneous distribution of the SiC particles in the

24 matrix of the solidified A356 composite. In addition, the sedimentation of the SiC particles decreases

1 at the semi-solid state stirring temperature[27], which can also result in a homogeneous distribution of

2 the SiC particles because of the presence of a solid phase]28[.

3 During the solidification process, instead, it is believed that the particle engulfment mechanism

4 governs the solidification process of the preform sample, rather than the particle pushing mechanism,

5 which is activated in the AR-SiC sample. Generally, it has been proven that the particle engulfment

6 mechanism results in the formation of isolated particles inside the grains of metal matrix during

7 solidification, and the particle pushing mechanism leads to the formation of agglomerated particles at

8 grain boundaries and in the last freezing zones of the solidified material [29].

9 ### 3.2.3. Solidification mechanisms

10 The current models addressing the incorporation of particles into a solidifying matrix can be

11 categorised into three classes: (i) the kinetic models that predict the velocity of the solid/liquid

12 interface which is critical for the transition from particle pushing to engulfment [30], (ii) the

13 thermodynamic models [31] which are closely related to classical heterogeneous nucleation theory

14 and (iii) the models based on the ratio of the thermophysical properties of the particles and the melt

15 [32]. The latter model predicts the incorporation ability in general, that is, a dependence of the

16 incorporation behaviour on the processing conditions. Any dependence on the morphology of the

17 interface is not included.

18 The models based on the thermophysical characteristics rely on the thermal conductivity of particles

19 and liquid using Equation (1) [33]. The subscripts p and l refer to properties of the particles and the

20 liquid, respectively.

21 $$K_p > K_l \text{ for engulfment} \tag{1}$$

22 The models based on heat diffusivity [34] characteristics are based on Equation (2) using the thermal

23 conductivity (k), the specific heat (c_p) and the density (ρ):

24 $$\sqrt{\frac{K_p \cdot \rho_p \cdot c_p^p}{K_l \cdot \rho_l \cdot c_p^l}} > 1 \text{ for engulfment} \tag{2}$$

1. These two models show that by enhancing the thermal conductivity of particles incorporated into the

2. liquid matrix, the possibility of particle engulfment through the grains of the solidifying matrix

3. increases owing to change of the interface shape from convex to concave [15, 16, 32, 33], facilitating

4. the engulfment of particle through the matrix during solidification [15]. In essence, the lower thermal

5. conductivity of the particles affects the temperature gradient ahead of solidification front and therefore

6. acts as a barrier to the removal of the heat necessary for further solidification and consequently

7. inhibits particle engulfment.

8. In this study, it is expected that the thermal conductivity of SiC particles encapsulated by graphene

9. shells is much larger than those which are not encapsulated, as a result of high thermal conductivity of

10. graphene shell covered SiC particles [35, 36]. This is because the thermal conductivity of graphene

11. shells on SiC particles is better conserved in bilayer and trilayer GNSs than in single layer GNSs [37].

12. According to Equations (1) and (2), this high thermal conductivity of the SiC particles in the preform

13. samples results in the incorporation of most SiC particles in grain interiors rather than at grain

14. boundaries, as shown in Fig. 4(c) and corresponding schematic illustration (Fig. 4(d)).

15. Fig. 4(e) represents a high magnification TEM image of the preform sample containing engulfed SiC

16. particles. The inset in Fig. 4(e) demonstrates the selected area diffraction (SAD) pattern obtained

17. from the selected disk-shaped region of Fig. 4(e), demonstrating that this region contains GNSs with a

18. preferred crystallographic relationship of $\square111\square_{Al}//\square0001\square_{GNSs}$ to the matrix. Fig. 4(f) shows the

19. schematic demonstration of Fig. 4(e), representing the presence of SiC particles encapsulated by

20. graphene shells and some disk-shaped GNSs dispersed in the matrix.

21. **3.3. Tensile properties**

22. Fig. 5 represents tensile properties of the preform and AR-SiC samples. Insets are sketches illustrating

23. the microstructure corresponding to different samples. As shown in Fig. 5, the tensile strength and

24. ductility of preform samples are improved by about 45% and 84% compared to AR-SiC samples,

1 respectively. These superior tensile properties are ascribed to the effect of three possible important

2 strengthening mechanisms: (i) the Orowan strengthening mechanism related to uniform distribution of

3 SiC particles not only at the grain boundaries but most importantly in the grain interiors as well, (ii)

4 enhanced dislocation density as a result of the large mismatch between the thermal expansion

5 coefficient of GNSs and the aluminium matrix and finally, and (iii) the fiber pull-out toughening

6 mechanism.

7 As illustrated in the schematic image of Fig. 4, the microstructure of the preform sample contains SiC

8 nano-particles encapsulated by graphene shells and some dispersed disk-shaped GNSs inside the

9 grains of the aluminium matrix. In fact, graphene sheets play two important roles in enhancing the

10 tensile properties of the preform sample. First, they reduce the susceptibility of SiC particles to

11 cracking as a result of the onion-like shells around these particles, as shown in Fig. 4(e, f). This, in

12 turn, enhances the threshold stress limit of the SiC particles cracking during tensile stress, resulting in

13 higher tensile properties especially tensile elongation of the preform sample (Fig. 5). Second, these

14 onion-like graphene shells around the SiC particles can block the movement of dislocation passing

15 through the matrix, and make it difficult to reach the grain boundaries at the low stress levels

16 associated with the higher yield stress of the preform sample (225 MPa) compared to the AR-SiC

17 sample (155 MPa). Along with this unique role of the onion-like graphene shells in hampering the

18 dislocation crossing the SiC particles through the matrix, disk-shaped GNSs dispersed within the

19 matrix can also take a same synergic role in hampering dislocation movement within the matrix.

20 **3.3.1. Strengthening models**

21 Equation (3) can be employed to measure the increment in yield strength ($\Delta\sigma_y$) of the processed

22 composite as a result of the interfering effect of disk-shaped GNSs with dislocations sliding on (111)

23 the slip plane of the aluminium matrix, provided that the particles cannot be sheared by dislocations

24 and are well-dispersed in the slip plane of the matrix phase[38]. In this equation, M (3) is the Taylor

1. factor for polycrystalline FCC alloys, G (25 GPa) is the shear modulus of the aluminium matrix, b

2. (0.25nm) is the magnitude of the Burgers vector of dislocation, ϑ (0.35) is Poisson's ratio, f (0.01) is

3. the volume fraction of the GNSs, d (10 nm) and t (3 nm) are the average diameter and thickness of at

4. least 100 disk-shaped GNSs measured using HRTEM analysis, respectively.

5.
$$\Delta\sigma_y^{Disk} = \frac{MGb}{2\pi\sqrt{1-\vartheta}}\left(\frac{1}{0.931\sqrt{\frac{0.306\pi d_t t_t}{f}}-\frac{\pi d}{8}-1.061 t_t}\right)\ln\frac{1.225 t_t}{b} \tag{3}$$

6. Calculated results from Equation (3), using the above-noted values, demonstrate that enhancement in

7. the yield strength ($\Delta\sigma_y^{Disk}$ = 229 MPa) of the preform sample as a result of disk-shaped GNSs is

8. significantly larger than the experimental values ($\Delta\sigma_y = \sigma_y^{Preform} - \sigma_y^{AR-SiC}$=70 MPa) obtained from

9. tensile tests (Fig. 5). This difference between predicted and experimental values for $\Delta\sigma_y$ as a result of

10. the Orowan strengthening mechanism can be attributed to the formation of graphene with two

11. different shapes including disk-shaped and onion-like morphologies. Indeed, the total volume fraction

12. (f) of disk-shaped GNSs was set to 0.01 during the above-mentioned calculation; however, as shown

13. in Fig. 4(e, f), graphene can also be found in the form of onion-like shells encapsulating SiC particles.

14. So, in order to clarify the weight of onion-like graphene shells encapsulating SiC particles in yield

15. strength increment compared to disk-shaped GNSs dispersed in the matrix of the preform sample, a

16. modified version of the Orowan strengthening mechanism applicable for round-shaped particles is

17. used in Equation (4)[38]:

18.
$$\Delta\sigma_y^{Onion} = \frac{MGb}{2\pi\sqrt{1-\vartheta}\left(\frac{0.779}{\sqrt{f}}-0.785\right)d}\ln\frac{0.785\,d}{b} \tag{4}$$

19. In this equation, all parameters have the same values as Equation (3) unless the d parameter, related to

20. the size of the onion-like graphene shells encapsulating the SiC particles through the matrix, is set to

21. 46nm, under this assumption that at least two graphene layers have covered the SiC particles. This

22. was calculated by investigating more than 100 nano SiC particles, with a diameter of 45nm and

13

1   provided there is no agglomeration of the SiC particles, and all pure GNSs have been converted into

2   onion-like shells. The results show that by considering these primary conditions, the maximum

3   enhancement in yield strength of the preform sample, as a result of onion-like graphene shells around

4   SiC particles, is limited to 58 MPa. This value is in good agreement with results of tensile tests with a

5   better approximation, making Equation (4) the main governing model for predicting tensile properties

6   of the preform sample. Indeed, these calculations demonstrate that the maximum increment is induced

7   due to the fact that the formation of disk-shaped GNSs particles through the matrix can be about 4

8   times ($\frac{\Delta \sigma_y^{Disk-shaped\ GNSs}}{\Delta \sigma_y^{Onion-liked\ GNSs}} = 3.95$) bigger than the one endued by onion-like graphene shells, evincing

9   the major role of disk-shaped GNSs in enhancing the yield strength of the preform sample. Therefore,

10   it can be seen that the achievement of a 45% improvement in the yield strength of the preform sample,

11   over that of the AR-SiC sample is attributed primarily to the higher contribution of onion-like

12   graphene shells encapsulating SiC particles. There are a number of reasons for the lower yield

13   strength of the preform sample compared to the values predicted by Equation (3) ($\Delta \sigma_y^{Disk} = 229$ MPa):

14   First, disk-shaped GNSs are assumed to have a habit plane perpendicular to the slip plane of

15   aluminium (111) in the model presented. However, in fact, GNSs lie on the slip plane of the

16   aluminium matrix. Hence, it is predicted that the amount of interaction between GNSs and dislocation

17   gliding on the matrix slip plane is lower than in the suggested model. Nevertheless, SiC particles

18   coated by onion-like graphene shells interact with slip planes more easily as a result of their three

19   dimensional circular shape, which means that they have at least some sections which interact with

20   most active slip planes during the deformation process. Second, it is also anticipated that the number

21   of GNSs which are able to survive agglomeration, to form the undesirable graphite structure during

22   the manufacturing process through Van der Waals interactions, is not as high as to have the strong

23   effect suggested by the model presented (Equation (3)). Finally, as shown in Fig. 4(e, f), disk-shaped

14

1   GNSs have not been dispersed uniformly throughout the entire matrix, making it hard for them to

2   interact with dislocation effectively.

3   On the other hand, it should be noted that in addition to the Orowan strengthening mechanism which

4   confers higher yield strength on the preform sample, there are other strengthening mechanisms which

5   play an important role in boosting the tensile properties of the composite produced. One of these is the

6   thermally induced dislocation generated via a considerable difference between the thermal expansion

7   coefficient of the aluminium and the graphene (α_{Al}=21.4×10^{-6}/k, $\alpha_{graphene}$=-6×10^{-6}/k at 300k [39],

8    $\alpha_{graphene}$=0.9×10^{-6}/k at 873-1073K [40]) during solidification. As shown in Fig. 4(e), there is a high

9   possibility in the formation of thermally induced dislocation through the matrix during solidification.

10   In addition to the above-mentioned strengthening mechanism, the other reason for the higher tensile

11   properties of the preform sample compared with the AR-SiC sample is related to the lower porosity

12   content (1.6% ± 0.3) introduced in the sample compared to the AR-SiC sample (4% ± 0.6). This lower

13   porosity content of the preform sample can be attributed to the milling of SiC particles with

14   aluminium powder that causes close contact between these powders and removes the air gap between

15   them.

16   **3.3.2. Fracture behaviour**

17   Fig. 6(a) and (b) show the fractographic image of the AR-SiC and preform samples after tensile tests,

18   respectively. As can be seen in Fig. 6(a), the fracture surface of the AR-SiC sample contains cleavage

19   surfaces (white arrow) and some big dimples (white circle), is responsible for the lower tensile

20   ductility of the AR-SiC sample, as compared to the preform sample. In fact, the agglomeration of

21   particles in the AR-SiC sample (Fig. 6(a) and (b)), especially at the grain boundaries, as a result of

22   particle pushing, can facilitate the cracking of these agglomerated particles under lower stresses, and

23   accommodate a low energy path along the grain boundaries (intergranular fracture) for crack

24   propagation resulting in the lower tensile properties of the AR-SiC sample. In fact, externally applied

1 load is generally transferred from particle-lacking zones to particle-rich zones in a composite, with the

2 damage being generated in particle-rich zones because of the higher stress concentration at small

3 strains [28]. Furthermore, agglomerated particles are suitable sites for damage accumulation and local

4 particle-rich zones are the most appropriate nucleation sites of cracks [1, 41, 42].

5 However, in the case of the preform sample, as shown in Fig. 6(b), no evidence of cleavage surfaces

6 or big dimples was observed on the fracture surfaces, demonstrating the ductile failure of the

7 transgranular mode. More importantly, as demonstrated by black arrows in Fig. 6(b), in addition to the

8 unique characteristic of GNSs in blockading dislocation within the grains, they also have another

9 interesting macroscopic feature for preventing crack propagation during the fracture process under the

10 fiber pull-out toughening mechanism. Under such circumstances, growing cracks encounter pull-out

11 fibers, increasing the energy needed for propagation by diminishing the load transferred from the

12 matrix to the dispersed reinforcements resulting in more ductility [43].

13 **3.3.3. Characterization of the SiC/Matrix Interface**

14 The properties of MMCs are affected significantly by the characteristics of the interface between the

15 matrix and reinforcement [44, 45]. Reinforcing particles are thermodynamically unstable and endure

16 reaction at the SiC /matrix interface, depending on processing temperature and time. Interfacial

17 reactions often cause the removal of desirable elements from molten alloy, increasing melt viscosity

18 and reducing castability [46]. SiC reinforcement is not stable thermodynamically in contact with

19 molten aluminium alloys and therefore, Al_4C_3 formation is expected depending on the temperature,

20 environment and other parameters [1].

21 Fig. 7 (a) and (b) show HRTEM images of the SiC /matrix interface in the case of AR-SiC and

22 preform samples, respectively. Formation of Al_4C_3 at $605^{\circ}C$ and in the presence of about 7 Wt. % Si is

23 difficult [43, 47], and consequently the detection of Al_4C_3 is not an easy task. However, the results

24 obtained, as shown in Fig. 7(a), indicate its formation at nanoscale (2-5 nm) with a rod-like structure,

as shown in right corner inset of Fig. 7(a). As seen in Fig. 7(a), in the case of the AR-SiC samples, the

Al_4C_3 layer is formed around the SiC particle while in the case of the preform sample (Fig. 7(b)),

Al_4C_3 is formed only in some damaged areas of GNSs (white arrows). As demonstrated by inset of

Fig. 7(b), the formation of Al_4C_3 has also been approved by SAD pattern taken from the damaged area

of graphene sheets encapsulating SiC particles. Therefore, in the former, the ability for load transfer

from the matrix to the SiC particles is reduced, while in the latter, it increases. Additionally, particle-

rich zones produced as a result of severe agglomeration in the AR-SiC sample, limit the flow of liquid

before complete solidification of the composite and therefore, the interfaces in particle-rich zones are

defective. Since these zones rapidly lose their load-bearing capability, the strength of the composite

containing agglomerated particles is lower than those without particle agglomeration [48]. In fact,

agglomerated particles contain many inner smaller particles without any contact with the matrix.

These inner fine particles are easily displaced on each other during loading due to a weak mechanical

bonding, leading them to being conjoined. There is an air gap between these fine particles in which a

defect-free interface could not be formed between agglomerated particles and matrix.

More importantly, it is anticipated that the interface between SiC particles and the surrounding matrix

is stronger in the preform sample than in the AR-SiC sample as a result of the rough and wavy surface

of the graphene shells encapsulating the SiC particles. Indeed, it should be noted that graphene will be

wrinkled during heating, as shown by the black arrow in Fig. 7(b), due to its different behaviour and it

will expand during cooling and solidification [49]. This rough topography of the interface augments

interfacial friction in the interfacial zone of the SiC particles and the adjacent matrix during sliding of

debonded particles in the fracture which, in turn, permits realisation of more toughness in the preform

sample.

Moreover, the wrinkling phenomenon during solidification of the composite can lead to the formation

of a low-defect interface between the aluminium matrix and the nano-particles, leading to an

increment in the tensile strength of the composite. Additionally, the Al_4C_3 layer around the SiC particles in the AR-SiC sample cracks easily because it has a greater likelihood of containing a flaw(s) which can initiate cracks and lead to a weaker interface.

4. Conclusions

This study proposes an innovative fabrication method, making use of encapsulating and high thermal conductivity promising features of graphene, for manufacturing aluminium-based composite reinforced with nano SiC particles. The former enables the agglomeration of nano SiC particles during powder milling and subsequent liquid processing to be diminished, and the latter made a useful change in the solidification mechanism from pushing to the engulfment of particles.

The augmented tensile properties of this composite can be ascribed mainly to the strengthening effect of the graphene sheets manifested in the form of onion-like encapsulating shells for the nano SiC particles dispersed throughout the aluminium matrix. Having considered the Orowan strengthening mechanism, two different models were investigated, emphasising the major role of nano SiC particles encapsulated by onion-like graphene shells in attaining greater tensile properties. This improvement is also attributed to thermally induced dislocation brought about by considerable difference in thermal coefficient expansion of the graphene and aluminium matrix.

The fractographic investigations have also demonstrated that higher tensile ductility of composites containing graphene can be ascribed to lower agglomeration of SiC particulates as well as fiber pile-up mechanism. The former reduces the dimple size and the latter augments the energy needed for crack propagation through the matrix.

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28   Figure captions:

29 Fig.1. (a) Morphology of Al-55 Wt. % SiC-12 Wt. % graphene powder and (b) high magnification
30   image of (a).

31 Fig.2. (a) HRTEM images of SiC particle encapsulated by trilayer GNSs, (b) TEM image of SiC
32   particles in composite powder and (c) elemental TEM x-ray map of (b).

33 Fig.3. FE-SEM micrograph of (a) AR-SiC and (b) preform samples.

34 Fig.4. TEM micrograph of (a) AR-SiC sample, (b) schematic representation of (a), (c) preform
35   sample, (d) schematic representation of (c), (e) high magnification image of preform sample
36   associated with selected area diffraction (SAD) pattern of specified region, and (f) schematic
37   representation of (e).

1   Fig.5. Stress-strain curve of AR-SiC and preform samples accompanied with schematic illustration of

2   their nanostructures.

3   Fig.6. Fracture surfaces of (a) AR-SiC and (b) preform samples.

4   Fig.7. TEM microstructures of a SiC particle showing SiC/matrix interface in the case of (a) AR-SiC

5   and (b) preform samples. The rod-like structure and SAD pattern of Al_4C_3 are representing in the

6   insets of Fig. 7 (a) and (b), respectively.

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21   Table1. Chemical composition of A356 alloy used in this study (Wt. %)

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Al	Si	Fe	Cu	Mn	Mg	Zn	Ti
Bal.	7.0	<0.2	<0.2	<0.1	<0.1	<0.1	<0.2

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