

Article

In Situ Synthesis of Core-Shell-Structured SiCp Reinforcements in Aluminium Matrix Composites by Powder Metallurgy

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Abstract: SiCp reinforced aluminium matrix composites (AMCs), which are widely used in the aerospace, automotive, and electronic packaging fields along with others, are usually prepared by ex situ techniques. However, interfacial contamination and poor wettability of the ex situ techniques make further improvement in their comprehensive performance difficult. In this paper, SiCp reinforced AMCs with theoretical volume fractions of 15%, 20%, and 30% are prepared by powder metallurgy and in situ reaction via an Al-Si-C system. Moreover, a combined method of external addition and an in situ method is used to investigate the synergistic effect of ex situ and in situ SiCp on AMCs. SiC particles can be formed by an indirect reaction: $4\text{Al} + 3\text{C} \rightarrow \text{Al}_4\text{C}_3$ and $\text{Al}_4\text{C}_3 + 3\text{Si} \rightarrow 3\text{SiC} + 4\text{Al}$. This reaction is mainly through the diffusion of Si, in which Si diffuses around Al_4C_3 and then reacts with Al_4C_3 to form SiCp. The in situ SiC particles have a smooth boundary, and the particle size is approximately 1–3 μm . A core-shell structure having good bonding with an aluminium matrix was generated, which consists of an ex situ SiC core and an in situ SiC shell with a thickness of 1–5 μm . The yield strength and ultimate tensile strength of in situ SiCp reinforced AMCs can be significantly increased with a constant ductility by adding 5% ex situ SiCp for Al-28Si-7C. The graphite particle size has a significant effect on the properties of the alloy. A criterion to determine whether Al_4C_3 is a complete reaction is achieved, and the forming mechanism of the core-shell structure is analysed.

Keywords: in situ reaction; SiCp reinforced aluminium matrix composites; mechanical properties; core-shell structure



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1. Introduction

Aluminium matrix composites (AMCs) are attractive materials for lightweight applications owing to their high strength-to-density ratio, good wear and fatigue resistance, and high-temperature mechanical properties. In particular, particulate-reinforced AMCs have been increasingly studied [1,2]. SiC particles (SiCp) have been identified as probably the most competitive and effective discontinuous reinforcement for Al and Al alloy matrices due to their high melting point, high stiffness, good thermal stability, good chemical resistance, and low coefficient of thermal expansion [3]. Almost all existing methods for preparing SiCp-reinforced AMCs use ex situ techniques, such as rheocasting [4], infiltration [5], melt-stirring [6], and powder metallurgy techniques [7,8]. Chen Z. Z. et al. produced SiCp-reinforced 2024 aluminium-matrix composites by powder metallurgy and studied their fatigue crack initiation and small crack growth behaviours [9]. Yang Y. et al. fabricated SiCp-reinforced A356 aluminium matrix composites by the ultrasonic dispersion of nano-sized SiCp in a molten aluminium alloy and found that the mechanical properties significantly improved even at a low weight fraction of nano-sized SiCp [10]. Hu Q. Y.

et al. fabricated A356-SiC and 6061-SiC composites by a vacuum-assisted high-pressure die casting (HPDC) process [11]. Additionally, extensive studies have been conducted on the Al-SiC interfacial structure and the effect of various preparation methods on interfacial reactions [12,13]. The Al-SiC interface between the reinforcement and matrix can effectively transfer load from the matrix to the reinforcement, which plays a crucial role in the deformation and service of SiCp-reinforced AMCs.

However, the disadvantage of ex situ techniques, such as interfacial contamination and poor wettability between ex-SiCp and the matrix, limits their application in aerospace and other advanced fields [14]. During the past decades, considerable research efforts have been made towards in situ fabrication, which is devoted to reducing incompatibility and interfacial pollution [15]. In addition, in situ synthesised reinforcements can obtain better thermodynamic stability, finer size, and a more uniform distribution compared to ex situ particles [16]. Thus, AMCs reinforced by in situ SiCp are expected to exhibit superior mechanical properties compared to those produced by conventional processes [11].

The in situ synthesis of SiCp has been studied by many scholars. Sha J. J. et al. synthesised in situ SiC by the reaction $2\text{ZrSi}_2 + \text{B}_4\text{C} + 3\text{C} = 2\text{ZrB}_2 + 4\text{SiC}$, and the mean sizes of ZrB_2 and SiCp were approximately 300 and 40 nm, respectively [17]. Ren R. et al. prepared SiC nanowhiskers from photovoltaic silicon waste, quartz sand, and coconut fibre, which is a novel, clean, and sustainable method of preparing SiC nanowhiskers [18]. Gustafsson et al. fabricated $\text{Al}_2\text{O}_3/\text{SiC}$ nanocomposites by a new technique involving the in situ synthesis of nano-sized SiCp, which contains two reactions: $\text{SiO}_2(\text{s,l}) + \text{C}(\text{s}) \rightarrow \text{SiO}(\text{g}) + \text{CO}(\text{g})$ and $\text{SiO}(\text{g}) + 2\text{C}(\text{s}) \rightarrow \text{SiC}(\text{s}) + \text{CO}(\text{g})$. The SiC particle size was significantly reduced compared to the $\text{Al}_2\text{O}_3/\text{SiC}$ microstructures fabricated through conventional powder processing [19]. Du X. F. et al. performed some research on in situ SiCp formation in an Al matrix [20,21]. They designed a liquid-solid reaction to realise the in situ synthesis of SiCp in an Al melt and prepared SiCp-reinforced Al-18Si alloys by applying the casting method. Then, multi-scale SiCp-reinforced AMCs were prepared by powder metallurgy. El Oualid Mokhnache et al. synthesised Al_2O_3 and SiC in situ from an Al-SiO₂-C system by reaction hot pressing, and the change in the Al_4C_3 phase and its effect on the properties were discussed [22]. Al_4C_3 is a brittle phase and leads to hydrolysis, which should be inhibited in AMCs. The effect of the Si content on Al_4C_3 transformation still needs quantitative investigation, and the critical conditions for the complete reaction of Al_4C_3 cannot be found if the content changes in Al-Si-C systems [23].

To make full use of their advantages, ex situ and in situ SiCp co-reinforced AMCs were prepared in this study. Furthermore, in situ SiCp-reinforced AMCs were synthesised for comparison. Based on the phase diagram, the composition of the Al-Si-C system was designed to determine the process conditions for AMCs with in situ SiCp reinforcement without Al_4C_3 . The effects of ex situ SiCp and in situ SiC on the evolution of the microstructure and mechanical properties were studied.

2. Experimental Procedure

2.1. Materials and Processes

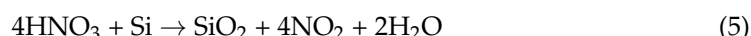
Commercial pure Al powder (99.0 wt% purity, diameter ~30 µm), Si powder (99.0 wt% purity, diameter ~30 µm), graphite powder (99.0 wt% purity), and polyangular SiC ceramic powder (98.5 wt% purity, diameter ~40 µm) were used in this study. To investigate the effect of graphite powder particle size on the properties, two sizes were applied; the average particles sizes were 6.5 and 10 µm, labelled G1 and G2, respectively. The fabrication processes of in situ SiCp reinforced AMCs mainly consisted of four steps. The first step was to mix the three powders for 4 h in an ethanol solution by planetary ball milling (PBM, PM-100, Retsch, Haan, Germany) at a rotation speed of 200 rpm and a ball-to-powder weight ratio of 3:1, and then the powder mixture was dried. The theoretically calculated volume fractions of in situ SiCp in the AMCs were 15, 20, and 30 vol%. Then, the powder mixture was compacted at room temperature in a 12.7 mm diameter die at a maximum pressure of 1500 MPa. The third step was sintering in a tube furnace for 2 h at 1000 °C

with a heating rate of 10 °C/min in an argon gas atmosphere. The sintered billets were subsequently re-sintered by spark plasma sintering (SPS, LABOX-330, Sinter Land, Niigata, Japan) at 570 °C at a pressure of 30 MPa for 30 min under vacuum conditions. During sintering, the following reactions may occur in Al-Si-C system:



Therefore, in this study, in-situ SiCp can be synthesised by indirect reactions via Equations (1) and (3) [24].

To prepare AMCs reinforced by ex situ and in situ SiCp, the mixed powder contained Al, Si, C, and acid pickled SiC in the first step. The difference between preparing in-situ SiCp reinforced AMCs lies in the treatment of powders and the first step; other steps were done under the same aforementioned conditions. The SiC particles were acid pickled by a mixed acid ($\text{HNO}_3:\text{HF} = 3:2$, vol%), 100 millilitres of mixed acid could pickle ten grams of silicon carbide, the concentration of HNO_3 and HF was diluted to a concentration of 10%. By pickling, the silicon atoms of the surface layer of SiC can be reacted away, exposing the carbon atoms. The reaction is as follows [25]:



The acid pickled SiC particles were washed with distilled water until the pH value of the cleaning solution was neutral, then dried in the drying oven. The mass fraction of the ex situ SiCp accounted for 5%. The AMC samples prepared are shown in Table 1.

Table 1. AMC samples prepared from different starting powders.

Sample	Al (wt%)	Si (wt%)	C (wt%)	Ex-SiC
Al-20Si-5C(G1)	75	20	5 (~6.5 µm)	Without
Al-28Si-7C(G1)	65	28	7 (~6.5 µm)	Without
Al-30Si-10C(G1)	60	30	10 (~6.5 µm)	Without
Al-20Si-5C(G2)	75	20	5 (~10 µm)	Without
Al-28Si-7C(G2)	65	28	7 (~10 µm)	Without
Al-30Si-10C(G2)	60	30	10 (~10 µm)	Without
Al-20Si-5C(G1)-5SiC	75	20	5 (~6.5 µm)	5 (~40 µm)
Al-28Si-7C(G1)-5SiC	65	28	7 (~6.5 µm)	5 (~40 µm)
Al-30Si-10C(G1)-5SiC	60	30	10 (~6.5 µm)	5 (~40 µm)

2.2. Characterisation

The sintered samples were characterised by X-ray diffraction (XRD-7000, SHIMADZU, Kyoto, Japan) with a Cu K α radiation source to identify the phases. The microstructure evolution of the composites and morphology of in situ synthesised SiC particles were observed by optical microscopy (OM-GX71, OLYMPUS, Tokyo, Japan) and field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Tokyo, Japan). The tensile properties of the samples were tested by a universal tensile testing machine (HT-2402, HUANG HE, Changchun, China).

3. Results

3.1. Microstructure

3.1.1. Morphologies of the Powders

SEM micrographs of the raw materials and premixed powder are shown in Figure 1. The Al particles were nearly spherical, as shown in Figure 1a, and the Si particles were irregular polygons, as shown in Figure 1b. In Figure 1c,d, an irregular layered structure existed in the raw graphite powders. Figure 1e shows the Al-Si-C premixed powder after PBM. It is shown that the Si particles and graphite particles both had small sizes and mainly adhered to the Al particles. It is deduced that the uniform dispersion of Al-Si-C mixed powders could be obtained by PBM for 4 h. The morphology of ex situ SiCp was irregular, as shown in Figure 1f.

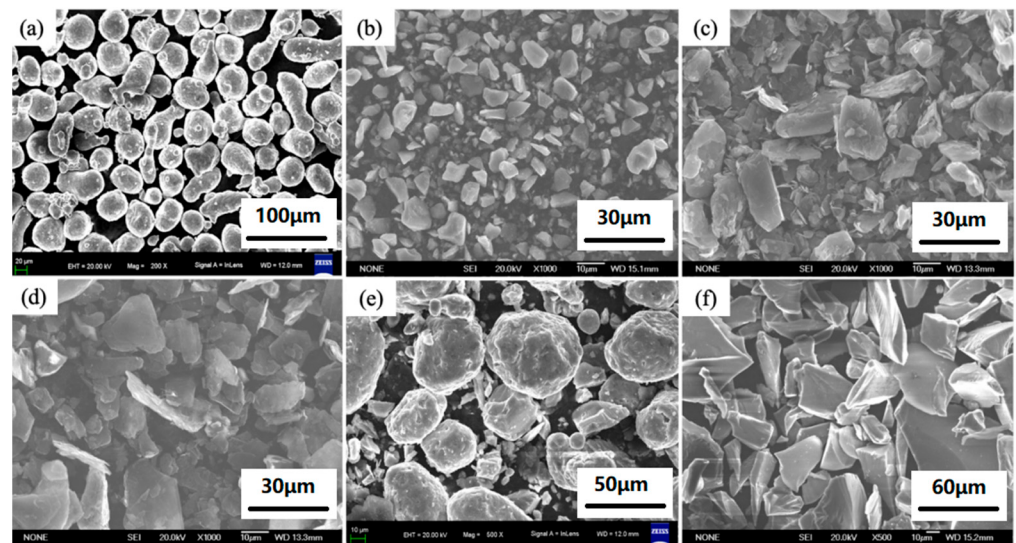


Figure 1. SEM images of the raw materials: (a) raw Al, (b) raw Si, (c) raw graphite 1 (G1), (d) raw graphite 2 (G2), (e) Al-Si-C premixed powder, and (f) ex situ SiCp powder.

3.1.2. Phase Analysis of the In Situ SiCp/Al-Si Composites

Figure 2 shows the X-ray diffraction (XRD) patterns of samples with different component ratios, as shown in Table 1. Clearly, a 3C-SiC diffraction peak was found, and the intensities of the diffraction peaks were enhanced with an increase in Si and C content. This indicated that a chemical reaction took place in the Al-Si-C system during the preparation process. The peak of 4H-SiC was detected, which suggested that the transformation of SiC crystal type may take place in the process of the in situ reaction. The XRD analysis results demonstrated that in situ SiCp-reinforced AMCs could be fabricated and that the proportion of in situ SiCp in the AMCs could be adjusted by changing the content of carbon and silicon. In addition, there was also a small amount of Al_4C_3 synthesised in Al-20Si-5C(G1) and Al-30Si-10C(G1), and no diffraction peak of Al_4C_3 was observed in Al-28Si-7C(G1). For the samples added with G1 or G2, a similar trend was reflected in XRD diagrams. The distribution of the different component ratios of composites in Al-Si-C ternary phase diagram at 1000 °C is shown in Figure 3 [26]. The distribution of Al-20Si-5C(G1), Al-28Si-7C(G1), and Al-30Si-10C(G1) was obtained by drawing auxiliary lines on the Al-Si-C ternary phase diagram. The components of Al-20Si-5C(G1) and Al-30Si-10C(G1) were closer to the L + SiC + Al_4C_3 area; however, the component of Al-28Si-7C(G1) was in the L + SiC area. Therefore, the XRD analysis results were basically consistent with the phase diagram. Compared with the samples without ex-SiCp, there was no significant difference in the XRD patterns except for the peaks of 6H-SiC from ex-SiCp.

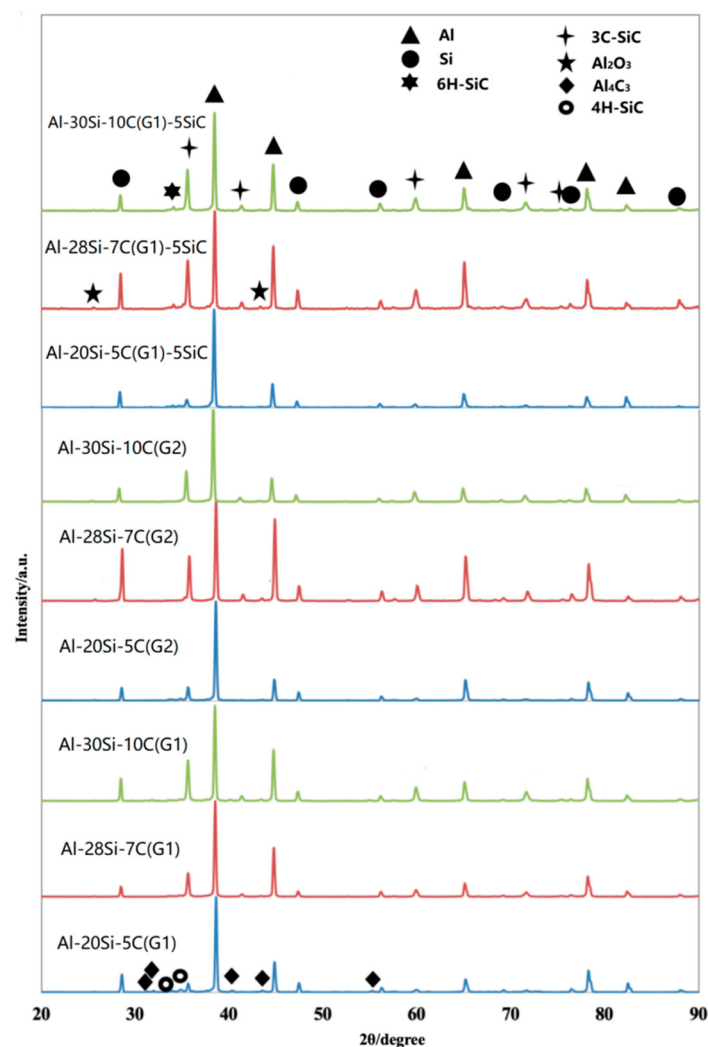


Figure 2. X-ray diffraction patterns of the samples with different component ratios.

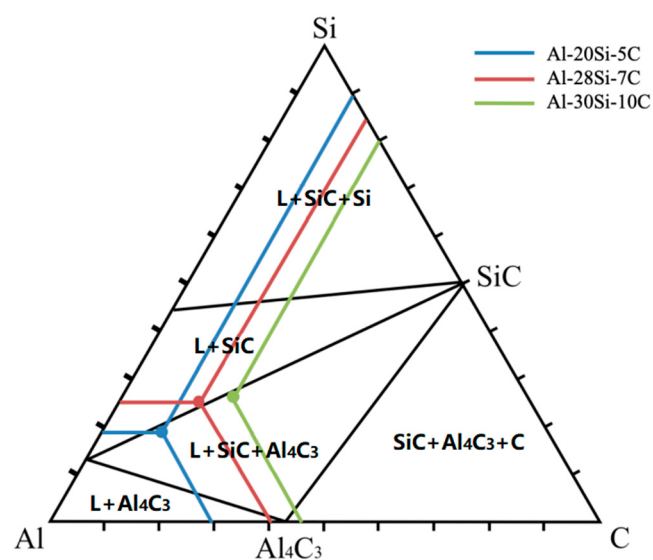


Figure 3. Distribution of the different component ratios of composites (Al-20Si-5C, Al-28Si-7C, Al-30Si-10C, wt%) in the Al-Si-C ternary phase diagram at 1000 °C [26].

3.1.3. Microstructure of In Situ SiCp Reinforced AMCs

Figure 4 shows the SEM photos of Al-28Si-7C(G1). The irregular particles with relatively bright colours are dispersed in the matrix with a light grey colour, and the particles are uniform. The EDS point scan analysis was performed at Spot 1, and the atomic ratio was close to 1:1, which confirmed that the particles were in situ SiC particles. To further observe the in situ SiC particles, in situ SiCp reinforced AMCs were deeply etched. Figure 5 shows the comparison between in situ SiC particles and the ex situ SiC particles. The ex situ SiCp is much larger than in situ SiCp in size. Both are irregular, and the difference is in their edges and corners. The ex situ SiCp has sharp edges and corners marked by the yellow circle in Figure 5a, and in situ SiCp has a relatively smooth boundary marked by the yellow circle in Figure 5b.

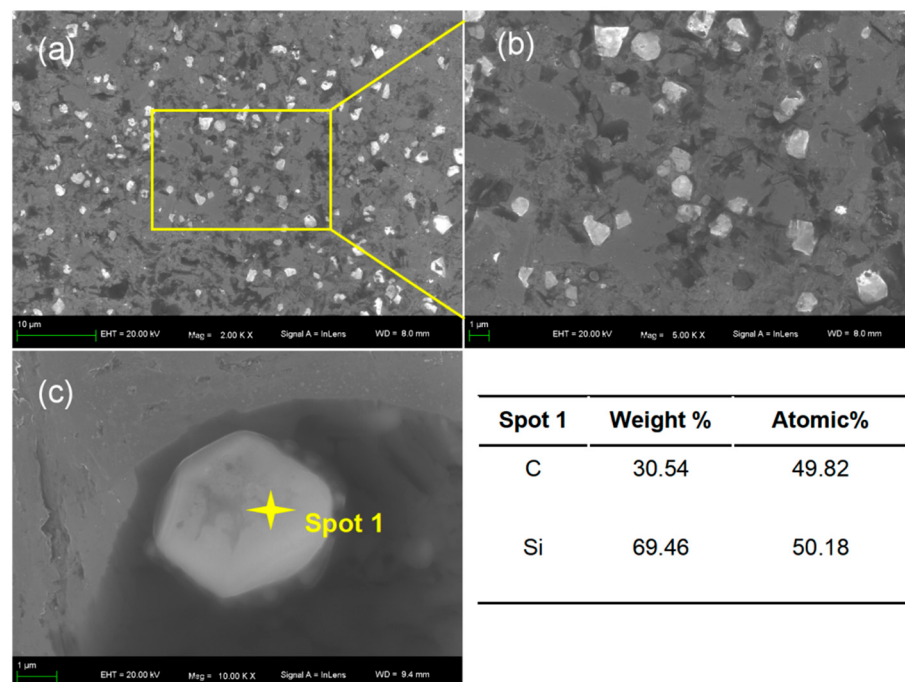


Figure 4. SEM images and EDS point scan analysis of Al-28Si-7C(G1): (a) SEM image, (b) SEM image, and (c) SEM image of Al-28Si-7C(G1) and EDS point scan analysis.

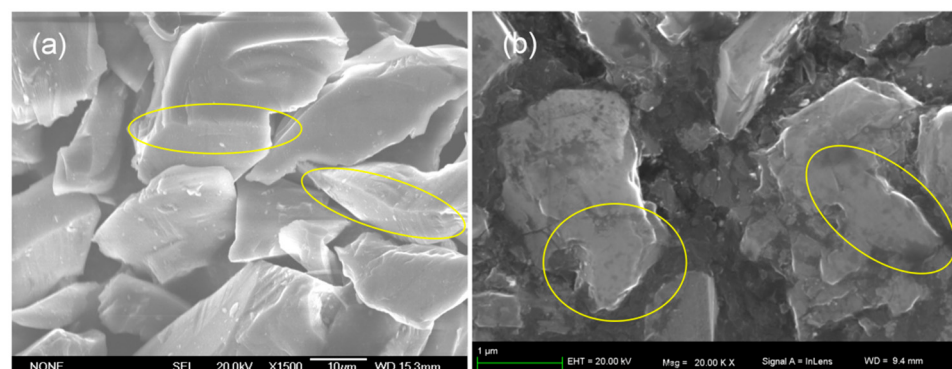


Figure 5. SEM images of ex situ SiC particles and in situ SiC particles: (a) Ex situ SiC particles, (b) In situ SiC particles.

3.1.4. Microstructure of Ex Situ SiCp and In Situ SiCp Reinforced AMCs

Figure 6 shows the SEM photos of Al-28Si-7C(G1)-5SiC. As indicated by the yellow arrows in Figure 6a, the ex situ SiC particles were clearly visible and surrounded by a light

layer with a thickness of approximately 1–5 μm , as shown in Figure 6b,c,e. The EDS point scan analysis was performed at Spot 1, as shown in Figure 6e. Only Si and C were detected at Spot 1, and the atomic ratio was almost 1:1, confirming it to be an ex situ SiC particle. Compared with Spot 1, the atomic ratio of Si and C at Spot 2 is also closed to 1:1, but there is a small amount of Al. Therefore, the layer with a light colour is considered to be an in situ SiC layer. In other words, a SiC core-shell structure can be formed, with ex situ SiCp in the centre surrounded by in situ SiC, which was achieved by adding ex situ SiCp into the Al-Si-C system.

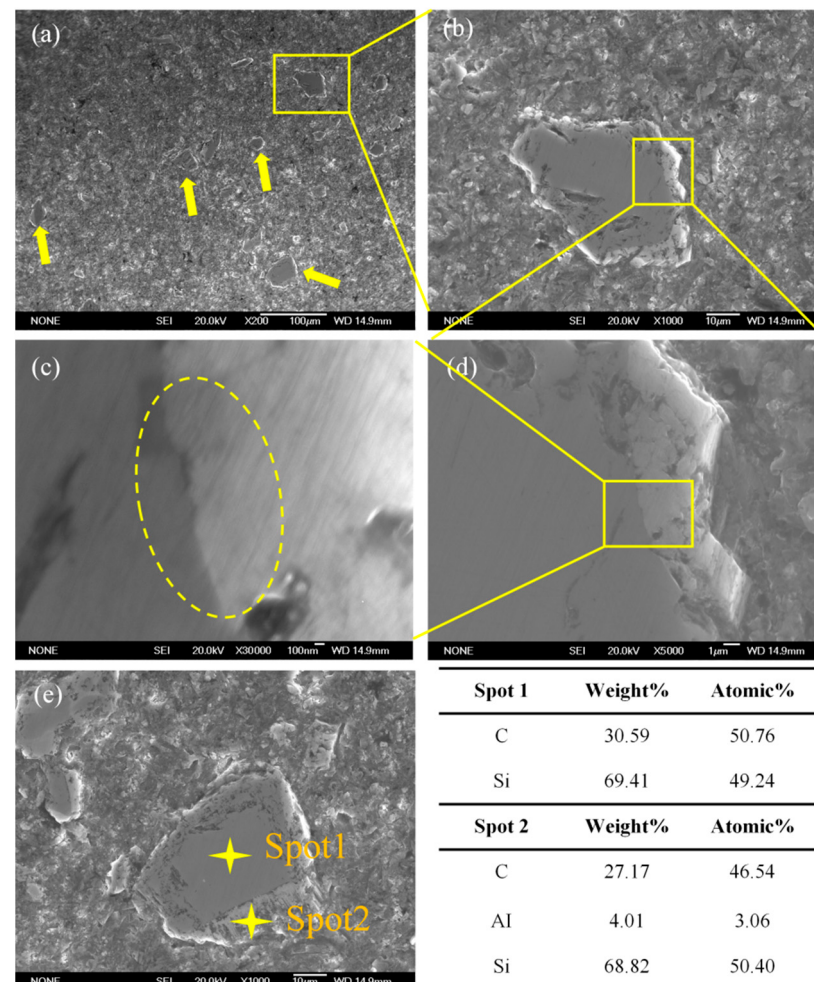


Figure 6. SEM images and EDS point scan analysis of Al-28Si-7C(G1)-5SiC: (a) 200X SEM image, (b) 1000 $\times$ SEM image, (c) 5000 $\times$ SEM image, (d) 30,000 $\times$ SEM image, and (e) EDS point scan analysis.

3.2. Material Property

3.2.1. Mechanical Properties of SiCp Reinforced AMCs

The mechanical properties of the samples are shown in Table 2. Al-30Si-10C(G1)-5SiC has the largest tensile strength and yield strength, but its plasticity is the worst. Al-20Si-5C(G1) has the best comprehensive mechanical properties, with a yield strength (YS) of 112 MPa, ultimate tensile strength (UTS) of 180 MPa, and elongation of 4.89%. To synthesise more in situ SiCp in the Al-Si-C system, additional Si and C are necessary, which leads to a decrease in Al content. The plasticity of SiCp-reinforced AMCs comes from Al, and the decrease in Al content is the main reason for the decrease in plasticity. Additionally, the in situ SiCp dispersed in the Al matrix contributes greatly to the strengthening of the composites. On the whole, the ultimate tensile strength and yield strength of SiCp reinforced AMCs with an average graphite size of 6.5 μm are higher than that of 10 μm .

The graphite powder size clearly affects the mechanical properties, and a smaller graphite particle size effectively improves the tensile properties of the in situ SiCp/AMCs when the content of silicon and carbon is low. However, for Al-30Si-10C, the ultimate tensile strength and yield strength increase when the average size of graphite is from 6.5 to 10 μm . Firstly, with the increase of silicon and carbon content, the uniform dispersion of particles becomes difficult. At the same time, the smaller the particles are, the easier agglomeration occurs. Secondly, the smaller the particle size is, the larger the surface area is, the more Al_4C_3 is formed, and the more unreacted Al_4C_3 is. Therefore, when the silicon and carbon content increase, increasing the graphite particle size can improve the ultimate tensile strength and yield strength.

Table 2. Yield strength (YS), ultimate tensile strength (UTS), elongation, and relative density of samples.

Sample	YS (MPa)	UTS (MPa)	Elongation (%)	Relative Density (%)
Al-20Si-5C(G1)	112 ± 2	180 ± 3	4.9 ± 0.5	99.38
Al-28Si-7C(G1)	128 ± 1	172 ± 2	2.1 ± 0.3	99.76
Al-30Si-10C(G1)	123 ± 1	167 ± 2	1.8 ± 0.3	97.11
Al-20Si-5C(G2)	109 ± 2	169 ± 2	4.6 ± 0.4	98.78
Al-28Si-7C(G2)	120 ± 1	156 ± 2	1.5 ± 0.3	99.59
Al-30Si-10C(G2)	138 ± 2	169 ± 1	0.8 ± 0.3	97.80
Al-20Si-5C(G1)-5SiC	113 ± 2	160 ± 3	3.3 ± 0.4	99.03
Al-28Si-7C(G1)-5SiC	141 ± 3	192 ± 3	2.1 ± 0.3	99.53
Al-30Si-10C(G1)-5SiC	211 ± 3	237 ± 2	0.6 ± 0.2	97.63

The tensile stress-strain curves of Al-20Si-5C(G1), Al-20Si-5C(G2), and Al-20Si-5C(G1)-5SiC are shown in Figure 7. It is interesting that an unusual change in the trend occurs for ex situ SiC reinforced AMCs. By comparing Al-20Si-5C(G1) with Al-20Si-5C(G1)-5SiC, it can be found that neither the strength nor ductility increase with the addition of 5% ex situ SiCp. There are few SiC core-shell structures due to the low contents of Si and C in the samples. Moreover, the size of ex situ SiCp is much larger than that of in situ SiCp, and the interfacial bond of the ex situ SiCp and Al matrix is not good without the SiC core-shell structure, which results in a decrease in the strength and ductility of the material.

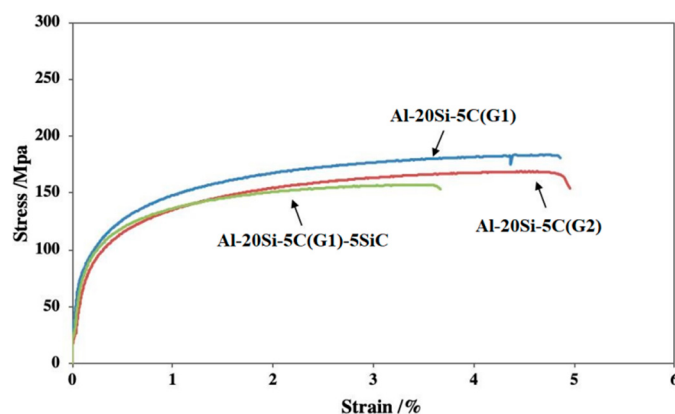


Figure 7. Tensile stress-strain curves of Al-20Si-5C(G1), Al-20Si-5C(G2), and Al-20Si-5C(G1)-5SiC.

The tensile stress-strain curves of Al-28Si-7C(G1), Al-28Si-7C(G2), and Al-28Si-7C(G1)-5SiC are shown in Figure 8. Compared with Al-28Si-7C(G1), the strength of Al-28Si-7C(G1)-5SiC is significantly increased with a constant ductility by adding 5% ex situ SiCp. With an increase in Si and C, additional core-shell structures are formed. In the core-shell structure, an in situ SiC layer is formed around the additional SiC particles, which not only realises the combination of SiC particles and the matrix at the atomic level but also blunts the sharp corners of the SiC particles and makes the original irregular particles rounder. Therefore,

for Al-28Si-7C(G1)-5SiC, the addition of 5% ex situ SiC increases the mechanical properties of the composite. As the content of Si and C increases, the strength of Al-30Si-10C(G1)-5SiC has a significant increase, and the ductility clearly decreases with the addition of 5% ex situ SiCp. The core-shell structure can increase the strength of Al-30Si-10C(G1)-5SiC, while the decrease in the aluminium matrix greatly reduces its plasticity. The strength can be improved without reducing the plasticity by optimising the proportion of in situ and ex situ SiCp.

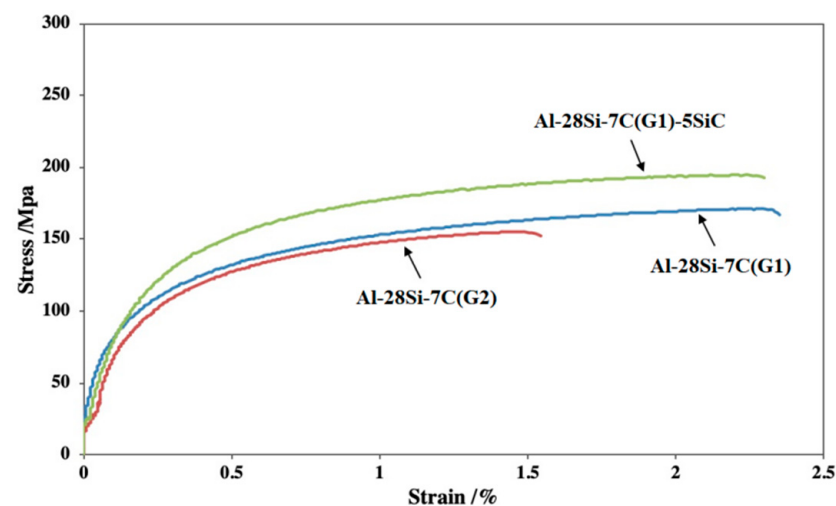


Figure 8. Tensile stress-strain curves of the SiC/AMCs.

3.2.2. Fracture Mechanism of the SiC Core-Shell Structure/AMCs

SEM images of the fracture surface of the tensile sample are shown in Figure 9. Hybrid-fracture characteristic appears in the fracture surface. Dimples and tear ridges have been observed, which are typical ductile fracture characteristics. Meanwhile, chevron cracking, marked by the yellow circle in Figure 9a, is a typical brittle fracture morphology. Chevron cracking is supposed to be produced from internal microcracks. In the region of large SiC particles, fracture is typical intergranular cleavage, as shown in Figure 9b, which indicates that the increase in Si content can decrease the plasticity of the material. The hybrid-fracture behaviour contributes to improving the mechanical properties.

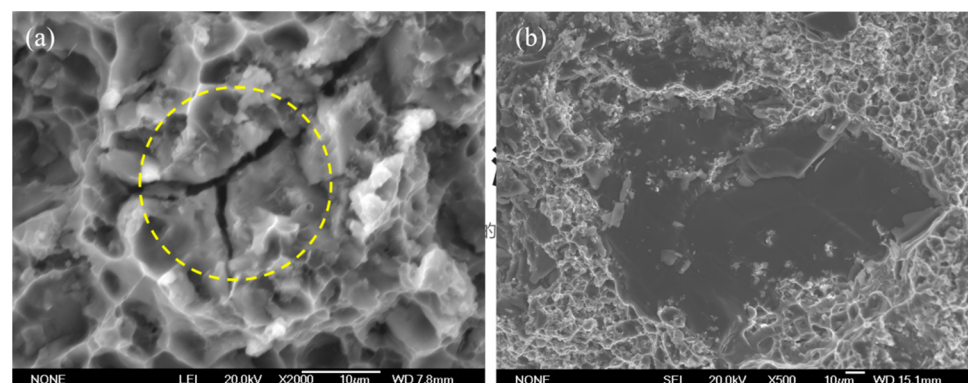


Figure 9. SEM images of the fracture surface of in situ SiCp-reinforced AMCs: (a) SEM image of Al-20Si-5C(G1) and (b) SEM image of Al-28Si-7C(G1).

As shown in Figure 10, the fracture mechanism of AMCs with the reinforcement of the SiC core-shell structure consists of ductile fracture of the Al matrix and cleavage fracture of the SiC core-shell structure. Some in situ SiCp with small sizes are found in the dimples shown in Figure 10c, which indicates classical particle-induced ductile fracture behaviour.

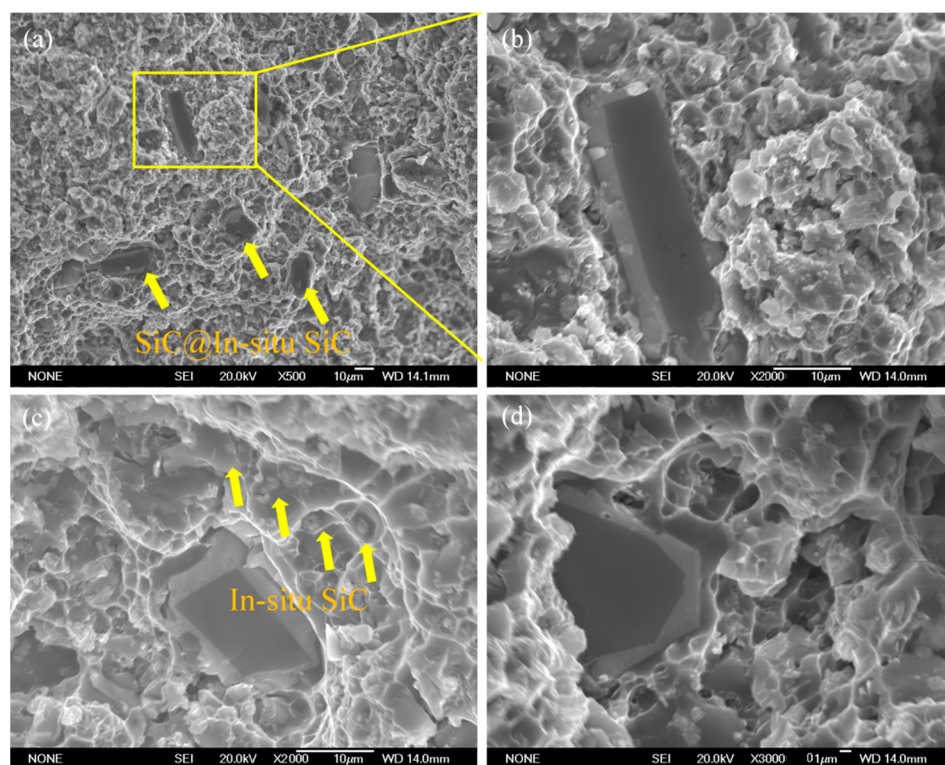


Figure 10. SEM images of the fracture of core-shell SiC (SiC@In situ SiC)-reinforced AMCs (Al-28Si-7C(G1)-5SiC): (a) SEM image of Al-28Si-7C(G1)-5SiC, (b,c) SEM images of Al-28Si-7C(G1)-5SiC, and (d) SEM image of Al-28Si-7C(G1)-5SiC.

4. Discussion

4.1. Conditions for the Complete Reaction of Al_4C_3

Through the analysis of the phase diagram in Figure 11, there is no Al_4C_3 above the AC line. Therefore, as long as the functional relations of the three components above the AC line can be found, it can be used as a criterion to determine whether Al_4C_3 is a complete reaction.

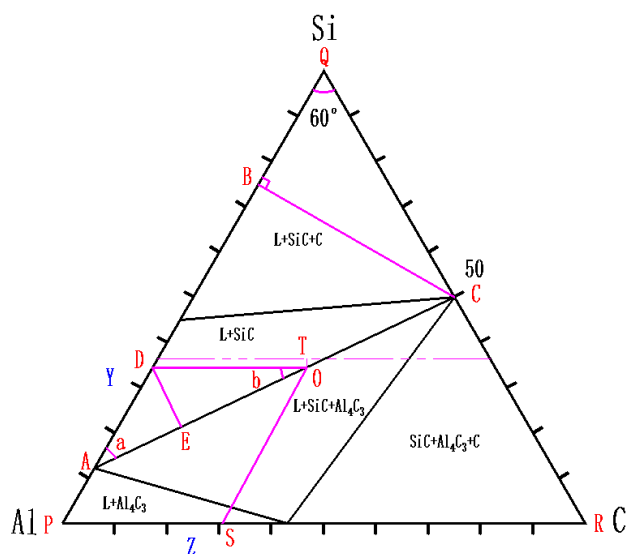


Figure 11. Al-Si-C ternary phase diagram at 1000 °C.

Taking any point O on the straight-line AC, let the mole percentages of Al, Si, and C in the alloy be X%, Y%, and Z%, respectively. It can be derived that the functional relationship of the AC line from the trigonometric relationship of triangle ADE, triangle ODE, and triangle ABC is as follows:

$$\sin \left(60^\circ - \arctan \frac{\sqrt{3}/2 \times QC}{100 - PA - 1/2QC} \right) = \sin \left(\arctan \frac{\sqrt{3}/2 \times QC}{100 - PA - 1/2QC} \right) \times (Y - PA)/Z \quad (7)$$

where QC is the mole percentages of Si in Al-Si components, PA is the mole percentages of Si in Si-C components.

If QC = 50 and PA = 12.2 are substituted into Equation (7), we obtain:

$$Y = 12.2 + 0.752 \times Z, \quad (8)$$

which indicates that the minimum mole percentage of Si without Al_4C_3 in the alloy is 12.2% when the Z value is zero. Conditions for the complete reaction of Al_4C_3 are to ensure that the component point is above the line AC, such as point T, so:

$$Y > 12.2 + 0.752 \times Z \quad (9)$$

Combined with the relationship $X + Y + Z = 100$ and substituted into Equation (9), we obtain:

$$Y > 49.88 - 0.429 \times X \quad (10)$$

and this formula is used for verification.

Only at the mole percentages of Al, Si, and C that satisfy Equations (9) and (10) simultaneously can Al_4C_3 be completely reacted to form SiC in an Al-Si-C system. Table 3 shows the verification comparison between theoretical calculation results and experimental results on whether Al_4C_3 is contained in Al-Si-C systems. For Al-20Si-5C and Al-30Si-10C, the mole percentages of Al, Si, and C cannot match Equations (9) and (10), so Al_4C_3 cannot be completely consumed, which is consistent with the XRD analysis results as shown in Figure 2. Therefore, Equations (9) and (10) can be used as the criterion for whether Al_4C_3 can be reacted completely.

Table 3. Verification comparison between theoretical calculation results and experimental results on whether Al_4C_3 is contained in Al-Si-C system.

Sample	X	Y	Z	$Y > 12.2 + 0.752 \times Z$ (Yes/No)	$Y > 49.88 - 0.429 \times X$ (Yes/No)	Theoretical Result	Test Result
Al-20Si-5C	70.6	18.8	10.6	No	No	With Al_4C_3	With Al_4C_3
Al-28Si-7C	60.3	25.1	14.6	Yes	Yes	Without Al_4C_3	Without Al_4C_3
Al-30Si-10C	53.4	26.7	19.9	No	No	With Al_4C_3	With Al_4C_3

4.2. Analysis of the Synthesised SiC Core-Shell Structure

Al-30Si-10C(G1)-5SiC was chosen to observe the core-shell structure more clearly due to its high carbon and silicon content and large graphite size. As shown in Figure 12a, there are many irregular particles with a light grey inside and a white edge, and the particle size is about 40–60 μm , indicated by the yellow arrow. One of the particles is magnified in Figure 12b,c. From Figure 12b, it can be found that there are many small spots (1–5 μm) around the SiC core-shell structure, such as Spot 2, which was tested by the EDS point scan analysis and proved to be in situ SiC particles because they have the same elemental composition as the in situ SiC layer observed at Spot 1. Figure 12c shows that part of the in situ SiC layer formed around the ex situ SiC particles is discontinuous, which is indicated by the yellow dotted circles. Therefore, it is considered that the nucleation and growth of in situ SiC formed around the ex situ SiC leads to the formation of an in situ SiC layer.

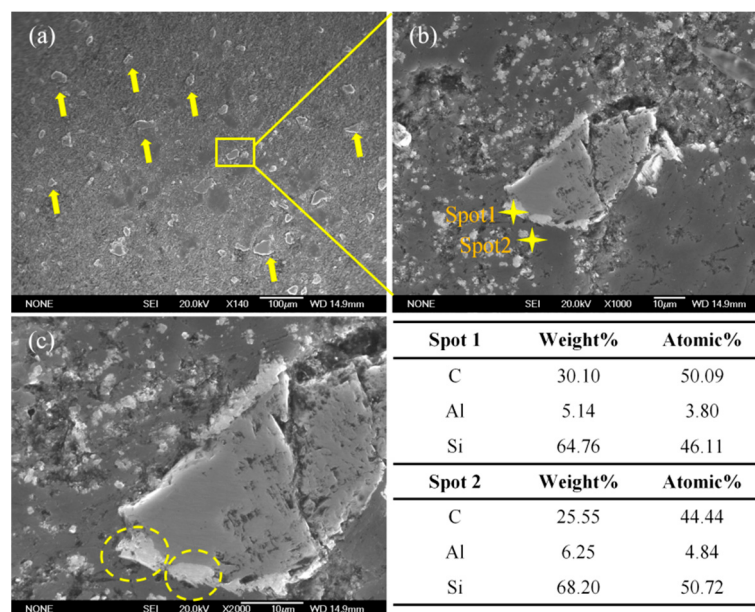


Figure 12. SEM images and EDS point scan analysis of Al-30Si-10C(G1)-5SiC: (a) 140× SEM image, (b) 1000× SEM image and EDS point scan analysis, and (c) 2000× SEM image.

Figure 13 shows EDS mapping of Al-30Si-10C(G1)-5SiC. It can be seen that there is only Si and C in the irregular particle area from the distribution of elements, and the content of Si decreases at the edge of the particle. Three points at the edge were selected for EDS point scan analysis. Spot 1 was on the edge of the particle, and the distance from Spot 2 and Spot 3 to the particle became farther in turn. At Spot 1, the content of Si and C is about 1:1, the content of Si is slightly lower, and there is a small amount of Al. When SiCp is added to a certain acid mixture of HNO₃ and HF, the Si atoms on the Si-terminated surface can react as chemical reactions 1 and 2. Thus, the C atoms on the Si-terminated surface are exposed. C will react with Al easily by the following chemical reaction: $3C + 4Al \rightarrow Al_4C_3$. Similarly, the C atoms on the C-terminated surface and the C atoms exposed on the Si-terminated surface because of the reaction of Si with the acids may also react with Al to form Al₄C₃ around the ex situ SiCp. The core-shell structure that SiC as the core and Al₄C₃ as the core can be recorded as SiC@Al₄C₃, where @ represents the core-shell structure. Then, Si atoms around the particles continue to react with Al₄C₃ to form SiC and Al through diffusion by the following reaction: $Al_4C_3 + 3Si \rightarrow 3SiC + 4Al$, so the Si content near the particles decreases and the Al content increases, which is consistent with the EDS point scan analysis of Spot 2. Spot 3 is relatively far away from the particles because the diffusion of silicon takes time, so the content of Si is slightly lower, which is close to the original composition. With the growth of the in situ SiCp formed around ex situ SiCp, the SiC layer is finally synthesised, thereby obtaining the SiC core-shell structure, recorded SiC@in situ SiC. Through the change of Si content around the core-shell structure, we can conclude that the formation of the core-shell structure is mainly completed by the diffusion of silicon. Figure 14 shows a schematic diagram showing the formation mechanism of the SiC core-shell structure.

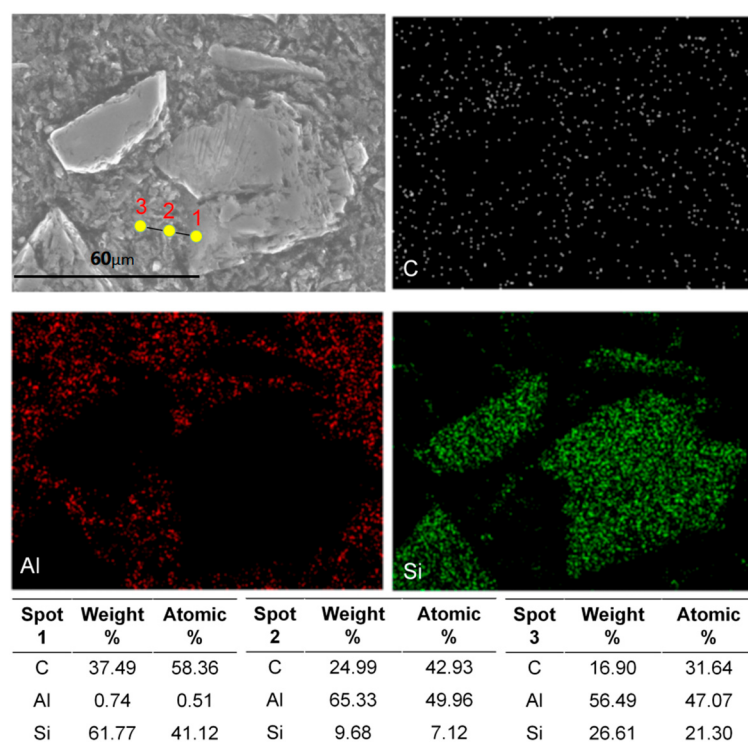


Figure 13. SEM image and EDS mapping analysis of Al-30Si-10C(G1)-5SiC.

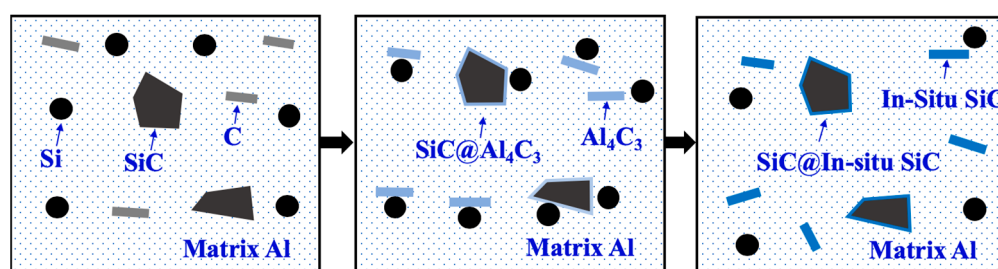


Figure 14. Schematic diagram showing the formation mechanism of the SiC core-shell structure (SiC@In situ SiC).

5. Conclusions

SiCp/AMCs were prepared with different volume fractions of SiCp by combining in situ synthesis and external methods. XRD analysis confirmed the existence of Al_4C_3 in the process of the in situ reaction and the two-step indirect reaction of SiC formation. SEM and EDS point scan analysis showed that in situ SiCp with a smooth boundary could be obtained via the Al-Si-C system by powder metallurgy and that the in situ SiC layer adhered to the added SiC particles, which closely coalesced with the original particles. Mechanical property testing showed that the elongation decreased by 50%, and the strength decreased by 12% when the volume fraction of SiC was increased from 15% to 20%. When the composite is Al-28Si-7C, the yield strength and ultimate tensile strength of in situ SiCp AMCs can be significantly increased with a constant ductility by adding 5% ex situ SiCp. The analyses show that there are few SiC core-shell structures when the content of Si and C is low. Moreover, the size of ex situ SiCp is much larger than that of in situ SiCp, and the interfacial bond of the ex situ SiCp and Al matrix is not good without the SiC core-shell structure, which results in a decrease in the strength and ductility of the material. With the content of Si and C increase, although a better core-shell structure can be formed, the elongation and plasticity still decrease because of the reduction of the aluminium matrix content. In the core-shell structure, an in situ SiC layer was formed around the additional

SiC particles, which not only realised the combination of SiC particles and the matrix at the atomic level but also rounded the sharp corners of the SiC particles, making the original irregular particles rounder. The formation of the core-shell structure is mainly formed by the diffusion of silicon through an indirect reaction: $4\text{Al} + 3\text{C} \rightarrow \text{Al}_4\text{C}_3$ and $\text{Al}_4\text{C}_3 + 3\text{Si} \rightarrow 3\text{SiC} + 4\text{Al}$. It is also found that decreasing the graphite powder size can improve the tensile properties of in situ SiCp/AMCs for Al-20Si-5C and Al-28Si-7C.

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