


Wettability in Metal Matrix Composites

Massoud Malaki ^{1,*}, Alireza Fadaei Tehrani ¹, Behzad Niroumand ² and Manoj Gupta ^{3,*} 

¹ Department of Mechanical Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran; mcjaft@cc.iut.ac.ir

² Department of Materials Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran; bezn@cc.iut.ac.ir

³ Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore

* Correspondence: m.malaki@me.iut.ac.ir (M.M.); mpegm@nus.edu.sg (M.G.); Tel.: +98-912-4424739 (M.M.); +65-6516-635 (M.G.)

Abstract: Metal matrix composites (MMCs) have been developed in response to the enormous demand for special industrial materials and structures for automotive and aerospace applications, wherein both high-strength and light weight are simultaneously required. The most common, inexpensive route to fabricate MMCs or metal matrix nanocomposites (MMNCs) is based on casting, wherein reinforcements like nanoceramics, -carbides, -nitrides, elements or carbon allotropes are added to molten metal matrices; however, most of the mentioned reinforcements, especially those with nanosized reinforcing particles, have usually poor wettability with serious drawbacks like particle agglomerations and therefore diminished mechanical strength is almost always expected. Many research efforts have been made to enhance the affinity between the mating surfaces. The aim in this paper is to critically review and comprehensively discuss those approaches/routes commonly employed to boost wetting conditions at reinforcement-matrix interfaces. Particular attention is paid to aluminum matrix composites owing to the interest in lightweight materials and the need to enhance the mechanical properties like strength, wear, or creep resistance. It is believed that effective treatment(s) may enormously affect the wetting and interfacial strength.

Keywords: wettability; metal matrix composites; MMCs; reinforcement



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1. Introduction

Metal matrix composites (MMCs) and metal matrix nanocomposites (MMNCs) are being employed in a variety of industries due to their exceptional tailor-made mechanical and tribological properties. Aluminum and magnesium-based composites are the most common metallic composites owing mostly to their light weight, good mechanical and tribological properties, low cost of the raw materials, as well as the flexibility and feasibility of producing them by different techniques [1–6]. In this paper the aim is to discuss the wetting in MMCs/MMNCs, but wettability here does not solely refer to the contact angle values being governed, for example, by surface tension; instead, all the efforts/strategies followed to improve the dispersion, engulfment, and distribution of reinforcing particles in a host metal matrix are also referred to as wettability.

The incorporation of reinforcing agents in metal matrices is preformed either by ex-situ or in-situ techniques. Unlike in-situ MMCs/MMNCs, ex-situ composites are more controllable as many parameters such as the weight fraction, shape and size of reinforcing particles, etc. can be determined and implemented. However, the main problem with the ex-situ MMCs is their relatively poor wettability. In-situ-produced reinforcements are usually more chemically wettable, kinetically stable, geometrically finer, tribologically cleaner, and uniformly distributed in a host metal matrix, compared to ex-situ MMCs [1,7,8]. As a result, the main focus of the present review is on those wetting improvement techniques employed for ex-situ MMCs.

Carbides, oxides, nitrides, borides as well as carbon allotropes are the most common reinforcements typically used to develop ex-situ MMCs and MMNCs. However, one of the greatest and challenging issues is the poor wettability between almost all nonmetal/metal interfaces [9,10]. Strong interfacial bonding either by mechanical interlocking or through chemical interactions between reinforcements and metals may significantly improve the mechanical properties, however, contaminants, imperfect bonding, detachments, cracks, voids or any other undesired intermetallic compound may drastically deteriorate the final performance [11]. Chemical composition, roughness, temperature and pressure conditions, atmospheric composition, surface chemistry (including surface oxidation, sintering aids, polarity, phases, anisotropy, and so forth) are some of the influencing factors, all strongly affecting the wettability [12–19]. Coarse, brittle interfacial reaction products are also usually detrimental and careful consideration should be paid to the microstructure. Bonding between metallic hosts and reinforcing particles can be metallic, ionic or covalent, among which the former is more desirable as the interfacial metallic bonds provide more ductile high-strength composites. Materials selection is vital in composite manufacturing as some reinforcing materials are adequately wetted by particular metals and hence an improved mechanical strength is expected. For instance, it was found that the ductility of TiC/Al composite is usually more than that of SiC/Al or Al₂O₃/Al owing to the formation of metallic bonds [20]. It has been reported that the production route can also be a determinant. For instance, some nanomaterials have been seen to be difficult to incorporate in molten metals (in casting for example) while they can be embedded in the same host matrix in solid or semi-solid states. Many surface modification methods such as electroless (autocatalytic) plating [21,22], ion implantation [23,24], plasma pulses [25], sintering metallization [26], mechanical stirring, etc. have also already been developed to improve the wettability in ceramic particles-reinforced metal matrix composites. Alloying with reactive elements such as Ti, Si, Mg, etc. has also been used to improve the affinity between non-metal reinforcements and metal matrices.

In term of the layout of this review, the wettability and the basics in metal matrix composite systems are introduced; the next step will be the most common and important ways to improve the wettability in metal-reinforcement interfacial regions starting with those thermal treatments and the temperature effect on adhesion and affinity in MMCs or MMNCs, pre- or post-mechanical treatments including stir casting or ultrasonication, reactive wetting processes to improve wetting conditions by chemical agents, as well as strategies based on coating reinforcements to provide composites with stronger interfacial and mechanical properties. It is to be noted that particular attention is paid on those aluminum matrix composites owing to the great interest in lightweight materials and the need to improve the properties like strength, wear, and creep resistance.

2. Wettability

Wettability is a measurement of the interfacial attraction between a liquid and another liquid or solid. It is the tendency of a liquid material to maintain contact with the surface of a solid material being governed by a force balance between adhesive and cohesive inter-molecular interactions. To date, innumerable materials with different wetting conditions have been developed and employed to strengthen MMCs and MMNCs; however, the wetting property of these nanomaterials are always a challenging issue in all composite manufacturing methods.

The sessile drop method is commonly used to determine the contact wetting angle between solids and liquids and is usually performed in a temperature range of 400–2000 °C [27]. Several important parameters including the surface roughness and the composition of the solid, the melted metal purity as well as the gas pressure and composition affect the contact angle. According to Young's model, schematically shown in Figure 1, the contact angle is determined by Equation (1) quantifying the wetting property of a solid by a liquid material [28].

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos \theta_C = 0 \quad (1)$$

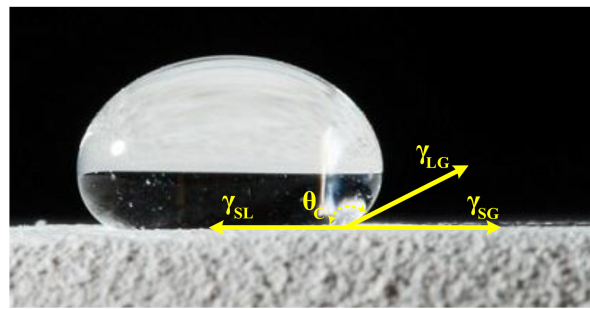


Figure 1. Young's model of wettability with three vectors of solid–gas, solid–liquid and liquid–vapor surface tensions.

In this equation, γ_{SG} , γ_{SL} and γ_{LG} respectively denote to solid–gas, solid–liquid and liquid–vapor surface tensions. θ_C is the contact angle. It is noted that Young's model ignores gravity.

According to the aforesaid equation, raising the solid–liquid interfacial energy, increasing solid surface energy, and diminishing liquid surface tension, all reduce the contact angle in solid–liquid interface being tantamount to better wettability.

The following equation presents the work of adhesion (W_a) described in terms of surface tension as well as wetting angle:

$$W_a = \gamma_{LG} + \gamma_{SG} - \gamma_{SL} = \gamma_{LG}(1 + \cos\theta) \quad (2)$$

To take into account the effect of volumetric dependence of the contact angle, the following modified Young's equation was proposed by Gibbs, wherein κ represents the line tension and a is the droplet radius [28–30]:

$$\cos\theta_C = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} + \frac{\kappa}{\gamma_{LG}} \frac{1}{a} \quad (3)$$

Further, the following equation considers the effect of Laplace pressure ignored in the Young's and the modified Young's equations [28–30]:

$$\cos\theta_C = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} + \frac{\kappa}{\gamma_{LG}} \frac{1}{a} - \frac{\gamma}{\gamma_{LG}} \left[2 + \cos(\theta_C) - 2\cos^2(\theta_C) - \cos^3(\theta_C) \right]. \quad (4)$$

Contact angle is a unique property for a given solid, liquid and vapor system, however, in reality it varies between the two maximal and minimal values due to contact angle hysteresis.

Wetting in MMCs/MMNCs between the reinforcement and the host metal matrix mostly relies on the following issues, among others:

Chemical reactions. No reaction between solid and liquid phases is generally recommended; minimum or no reaction/interdiffusion in the interfacial region, no degradation of reinforcing particles is usually desirable in almost all metal matrix composites or nanocomposites.

Contaminants. In general, oxides that appear on the reinforcement surface usually reduce the wetting of reinforcing particles by molten metals as the reinforcement engulfment by melt metals would be difficult, especially when the reinforcing phasis added from the top of the melt [31]. It is therefore recommended that any hindering oxide films be removed first if their existence might weaken the contact in solid–liquid interfacial regions.

Surface roughness. Wettability is influenced by different parameters such as the surface roughness, which greatly influences the wetting behavior. Roughness ratio is usually calculated as the ratio between the areas of projected and actual solid surfaces. It is believed that surface roughness increases wetting angle in transition metal carbides [21,32]. It is commonly referred to Wenzel state if a given solid (e.g., reinforcing particle) is perfectly

wetted by a liquid material (e.g., melt metal) wherein the surface roughness boosts the wettability. However, it is referred to Cassie-Baxter state when the solid surface is heterogeneously wetted. The contact angles predicted by the Wenzel and Cassie-Baxter equations have shown good agreement with those measured from real surfaces.

Gas layer. Importantly, it was shown that the gas layer if it covers a ceramic particle [33] being presumably one of the most important reasons for poor wettability and the reduced affinity between the reinforcement and matrix [34,35] preventing the molten metal to come in the contact with the reinforcing phase.

Density. The reinforcing particles may sink to the melt bottom or float to the top surface depending on density.

Temperature and pressure. A change in temperature may alter the contact angle significantly [31]. Table 1 presents the wetting behavior of SiC-, B₄C-, and Al₂O₃-filled aluminum matrices wherein an increase in temperature may lead to a decrease in contact angle and hence a better wettability could be achieved. Furthermore, the wettability sharply increases at temperatures above ~900 °C when the oxide layers are also broken and the melt metal could completely diffuse through the oxide films. It was also seen that the wetting angle is not greatly affected by pressure.

Time of contact. Wetting kinetics can be greatly influenced by the interaction time between the melt and its reinforcement. For instance, An et al. [30] measured the contact angle of pure Al-SiC system as 106° at 1173 K, reaching to 85° only after a contact for 8 min at the same temperature, attributed to the disruption of oxides and the self-cleaning reactions of the aluminum melt. Aguilar et al. [36] studied the Al-TiC system, and emphasized that each of the three wetting steps needs enough time. While a shorter time may not provide enough interfacial strength, excessive amount of contact time may also be detrimental leaving some unwanted products. The time of contact has to be adjusted during melt treatments as well; for example, mechanical stirring for too long may result in turbulence with consequent porosities, voids and gases being entrapped from the atmosphere [37,38].

Table 1. Contact angle of ceramic particles in aluminum of different temperatures.

Ceramic Phase	Temperature (°C)	Contact Angle (°)	Pressure (Torr)	Refs.
SiC	900	150	2.7×10^{-4}	[35]
	1100	34	1.5×10^{-5}	[39]
	1100	42	2.7×10^{-4}	[40]
B ₄ C	900	135	$10^{-5} \times 10^{-6}$	[41]
	1100	120	$10^{-5} \times 10^{-6}$	[41]
	1100	119	1.5×10^{-4}	[42]
Al ₂ O ₃	900	90	2.6×10^{-5}	[42]
	900	120	10^{-5}	[43]
	1100	70	2.6×10^{-5}	[42]
	1100	80	10^{-4}	[43]
	1100	83	10^{-5}	[44]

Particle size. As the particle size decreases to micro- or even nanoscale, wetting may become difficult very since: (i) small particles have extremely high surface areas and hence a great tendency to agglomerate is created due to interparticle forces such as van der Waals attraction; (ii) the metal melt needs more energy to deform to a small radius so that the particles could penetrate into it [31]. To date, different approaches are taken to improve the wetting at the matrix-reinforcement interfacial region, trying mostly to increase the particle energy, decrease surface tension and solid-liquid interfacial energy [8,31,45–47].

Materials and crystallinity. It was proved [48] that the crystallographic orientation of α -Al₂O₃, i.e., R (0112), A(1120) and C(0001), strongly affects the wetting and adhesion between the alumina surface and the corresponding aluminum melt over the temperature range of 800–1500 °C under the protection of Ar-3%H₂; as shown in Figure 2. The measured

adhesion was very strong on the R (0112) & A (1120) surfaces than on C (0001) surface owing to the oxygen-termination of R and A surfaces and aluminum-termination of the C surface.

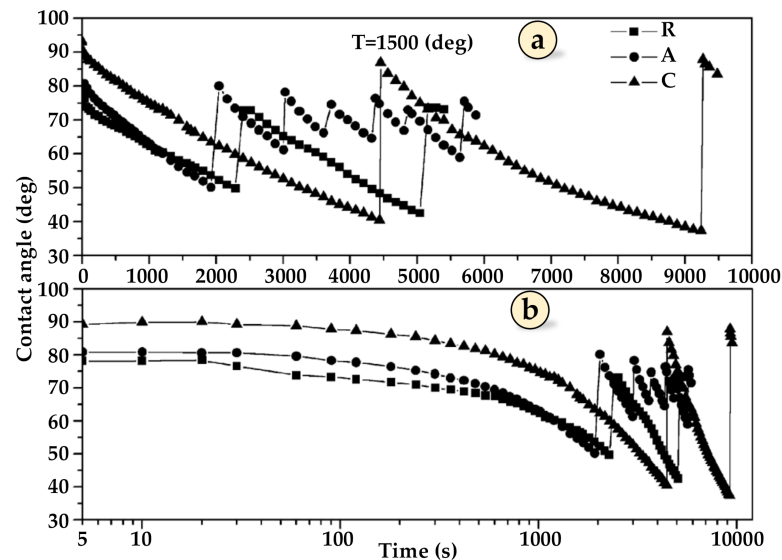


Figure 2. The effect of crystallographic orientation of $\alpha\text{-Al}_2\text{O}_3$, i.e., R (0112), A (1120) and C (0001), on the wetting and adhesion, reproduced from [48] with permission of Elsevier, 2003. (b) is the logarithmic time scale of (a), showing a maximum contraction at ~ 30 s.

3. Thermal Treatment and Temperature

Heat treatments play a pivotal role in composite manufacturing. Thermal treatments are mainly divided into three distinct categories, with the first based on the treatments before adding reinforcing particles to the melt and the second mainly based on thermal processes when the solid particles have already been added to the liquid phase, and finally the third is based on solidification process of cast composites.

Reinforcement pre-heating process could bring a lot of advantages among which the desorption of moisture/gases [49], reduction of surface impurities or contaminants, improved particle retention [50], as well as modified particle surfaces [51] are the most important privileges. Regulating the temperature and adjusting the time of interaction between the reinforcing agent and melt metal/alloy are also very significant. The favorable effect of pre-heat treatment of SiC-filled aluminum matrix composites has been emphasized in different studies [21,31,52–54]. By thermal treatment of SiC, a layer of SiO_2 oxide has been observed growing on the surface of SiC particles to protect the filler material from the aluminum melt attack; the reaction between the aluminum melt with the in-situ formed oxides may improve the wetting conditions [31,52]. According to Tekmen et al. and Hashim et al., it was seen that a pre-heat treatment of SiC particles at temperatures about 900°C may lead to the formation of surface oxides (SiO_2) having better wetting with aluminum melts [21,31]. Wang et al. [53] compared the effect of thermal treatment (i.e., oxidation of SiC) with Ni-coating of SiC particles and concluded although both techniques can improve the wettability and hence better mechanical properties are achieved, the oxidation of SiC reinforcement (to produce SiO_2 with better wettability with Al) has a positive influence on the wettability as the measured tensile and compressive strength values of SiC/ SiO_2 /Al, are boosted by $\sim 7.51\%$ and $\sim 24.90\%$, respectively, as compared to those of Ni-coated SiC reinforced Al matrix composites.

Temperature and the time of treatment are to be carefully regulated and adjusted in all cast MMCs or MMNCs. It has been frequently reported that the melt temperature may influence the wetting angle as the reaction products at the reinforcement-metal interface is governed by temperature [54,55]. Figure 3 shows the contact angles at different temperatures between SiC and a variety of pure elements, i.e., Fe [56,57], Si [58,59], Al [14,22,60,61],

Cu [62–64], Ni [56,65], Ge [56,66], Co [56], Sn [56,67], Ag [56,68], Au [59,69] and Pd [23,56] indicating a strong dependency of contact angle on the melt temperature.

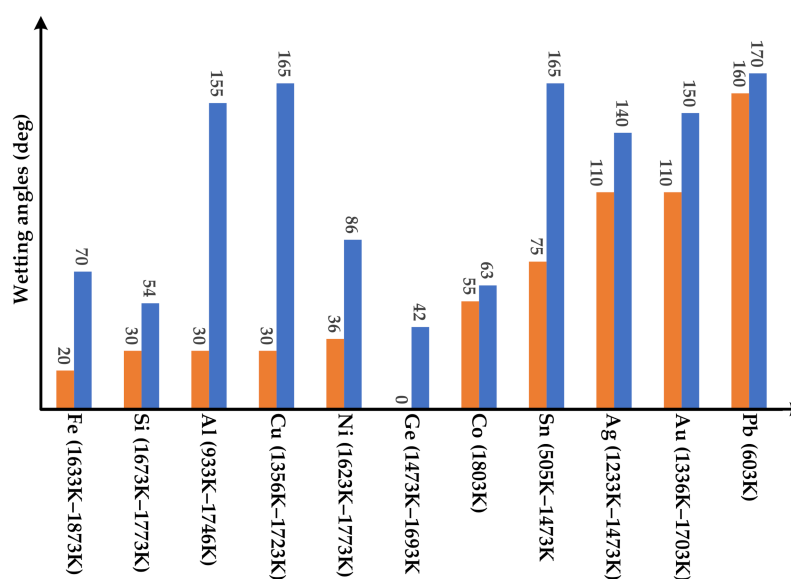


Figure 3. Minimal and maximal wetting angles (deg) at different temperatures for SiC reinforced pure elements.

In usual, an increase in temperature may lead to an improved wettability of SiC-reinforced aluminum matrix composites, e.g., through the disruption of the oxide layers; however, it synchronously could promote the formation of unwanted brittle carbides like Al_4C_3 in aluminum matrix composites deteriorating final properties especially ductility and toughness values [30,70].

Contact angle usually reduces over a longer time; however, some unwanted products may appear at higher temperatures or after longer interaction times. For instance, SiC is unstable in temperatures exceeding 1000 K, reacting with aluminum to expel silicon and form Al_4C_3 [35,71]. Salvo et al. [72] provided the required amount of silicon as a function of temperature in the melt matrix preventing the formation of aluminum carbide (for example, ~6.0 wt.% at 1000 K and 11 wt.% at 1100 K are needed to avoid Al carbide). Carbon-based nanomaterials are also usually poorly wetted by aluminum at the temperatures below 1000 K, but it is wetted above ~1270 K leaving, in turn, aluminum carbide being detrimental for mechanical performance [73]. It has been reported that some unwanted intermetallics, such as aluminum carbide, grow in graphite/Al system at temperatures > 1023 K for more than 2 h contact duration [74].

An et al. [30] found that the measured contact angle of pure Al-SiC system was initially ~154° at the temperature of 1003 K and a vacuum of 10^{-4} Pa implying the existence of oxides on the aluminum surface preventing full wetting to be achieved while the angle rapidly starts to decrease while increasing temperature where the value of 106° was obtained at 1173 K. Surprisingly the angle reaches to 85° after 8 min at the same temperature probably owing to the disruption of oxides and the self-cleaning reaction of aluminum melt (i.e., $4\text{Al}_{(l)} + \text{Al}_2\text{O}_{3(s)} = 3\text{Al}_2\text{O}_{(g)}$) [30]. It is therefore concluded that the wettability can be greatly affected by the interaction time between melt and reinforcement.

Figure 4a,b depict how the wetting angle of Al-SiC systems decreases as the interaction time of reinforcement-melt increases. It should be noted that the reduction of contact angle at higher temperatures usually happens in a shorter time than that obtained at lower temperatures, as demonstrated in Figure 4c.

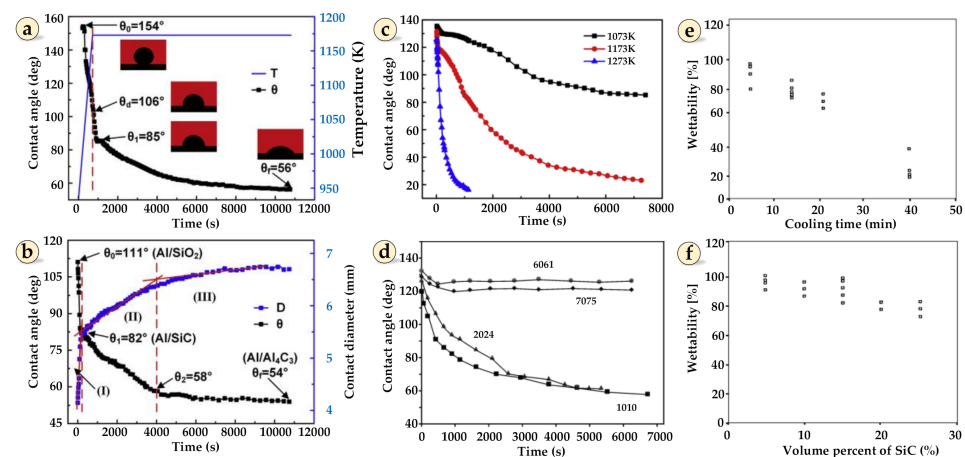


Figure 4. Variation of contact angle of Al-SiC system with time during (a) conventional sessile test [30], (b) isothermal dwelling at 1173 K by a dispensed sessile experiment. Herein, D represents the drop diameter [30]. (c) the variation of contact angle against time at different temperatures for Al-3.0 wt.% Ti alloy on SiC substrate [30]. (d) the variation of contact angle versus time in Al-TiC system at 900 °C [36]. (e,f) the effect of solidification time of SiC reinforced aluminum matrix composite on wettability [50].

According to Aguilar et al. [36], the reduction of contact angle in Al-TiC system happens in the three steps: (i) deoxidation of the Al drop, (ii) change in wetting kinetics due to chemical reactions followed by (iii) a plateau steady state. The time needed for each period depended on the matrix material and the type of reinforcing agent. Figure 4d also demonstrates the alloying elements in 7075 and 6061 alloys increase the tenacity of oxide films making them difficult to breakup even after an extended time interval. As seen, increasing temperature leads to a promoted wetting condition in most of solid-liquid systems. Levi and Kaplan [75] and Yu et al. [76] noticed a sharp transition from non-wetting to wetting situation while others like Sangghaleh and Halali [77] reported a gradual decrease in wetting angle. The differences in this trend may be attributed to the different processing conditions, materials and the chemistry of reinforcing agents with molten metals.

Even after applying different techniques to improve wetting, such as heat and mechanical treatments, a variety of reinforcing materials like ceramics and carbides are still poorly wetted and dispersed in a melt metal. These particles are usually rejected from the melt when the melt slurry starts to solidify leading to agglomeration, segregation, etc. To further improve or maintain the dispersion quality of reinforcing particles in these composites, the speed of solidification has been found to be a key factor as the reinforcement engulfment can be drastically improved if the solidification speed is high enough. Quicker solidification was found to have a positive influence on particle distribution and that the semi-solid solid casting routes seems better than full melting state in composite manufacturing [78]. It was seen that a rapid solidification may retain the particle locations in the bulk composites [79]. As shown in Figure 4e,f, Hashim et al. [50] studied the solidification speed of SiC reinforced A359 matrix composite to see the effect of solidification speed. A decrease in cooling time led to the formation of a higher percent of primary solid phase of α -Al nuclei and hence the higher volume fractions of reinforcing particles to be mechanically entrapped in the solidified composite as depicted in Figure 4c. Furthermore, they also confirmed that stirring is required to incorporate SiC reinforcements into the aluminum matrix. They believed that stirring under fully liquid conditions resulted in nearly zero wettability and no particle entrapment, while stirring in a semi-solid state could bring better wettability.

4. Mechanical Treatment

Mechanical agitation is a cost-effective, simple and productive method of achieving better wettability in most ceramic/metal composite systems [52]. Different types of elec-

tromagnetic [80], ultrasonic [81], and mechanical stirrers [82,83] are employed in order to incorporate reinforcing particles to a given metal matrix. Stirring is frequently used to improve wetting, deagglomerate reinforcing particles, improve homogenous distribution, expedite interfacial reactions, and reduce porosities and gases entrapped in solid-liquid interfacial regions, among others [52,80,82–86].

In all stir casting processes of MMCs or MMNCs, the stirring time and speed, impeller (size, shape and position in the melt), shear rate, shear period, cooling rate and the volume fraction of primary solid are of significant importance [78,87–89]. The optimum diameter (d) and optimum width (b) of the stirrer have respectively been reported as $0.4D$ and $0.1–0.2D$ where D is the crucible diameter [90].

Figure 5a illustrates a number of impellers commonly used in composite manufacturing. Naher et al. [78] and Moon [91] found that stirring with higher shear rate and shorter times could bring finer grains in conventional composites; in addition, less spherical particles have been found to be more easily entrapped by the solidification front due to additional drag created by those irregularly shaped micro-reinforcing particles [78].

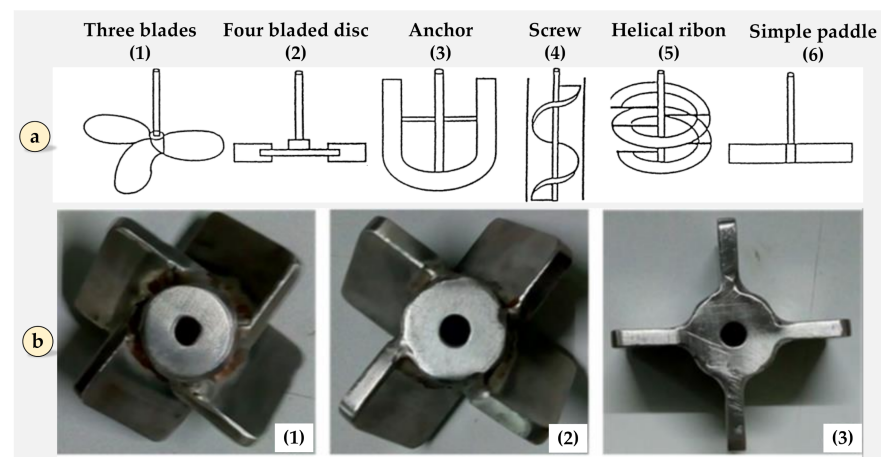


Figure 5. (a) Different types of stirring impellers, (b) the different angles of stirrer blade with (1) 45° , (2) 60° and (3) 90° reproduced from [84], with permission of Springer, 2020.

Many efforts have hitherto been made to study the effect of different stirring process conditions on the materials and mechanical performance of metal matrix composites [37,38,83–85,92–94]. Regarding impeller configurations, Torotwa and Ji [93] simulated a K_2SO_4 /water system mechanically stirred by four different impeller configurations, viz. anchor, counter-flow, saw-tooth, and Rushton turbine to predict the streamlines in different configurations. Based on a CFD simulation and a series of experiments, Krishnan et al. [83] reached the conclusion that the four-blade flat stirrer design is the best configuration amongst all others to achieve the best microstructural and mechanical properties in aluminum matrix composites. The mentioned finding has also been confirmed by others wherein the four-blade impeller has been recommended for its high performance [86].

Blade inclination has been found to be a key factor influencing the dispersion and the distribution of solid particles in a given melt. Using a commercial software, i.e., ANSYS Fluent 18.1, Mehta and colleagues [84] observed that the effect of stirrer blade inclination is more significant than that of stirrer position and these two in turn are more influencing than stirring speed. The stirrer speed of 400 rpm (among 300, 400 and 500 rpm), the blade angle of 45° (among 45° , 60° and 90°) and the stirrer position of 40% of height from the bottom of crucible (among 20 mm, 30 mm, and 40 mm from the crucible bottom) have been reported as the best stirring settings. With a lower stirrer position in the melt, the solid particles on the upper regions tend to float and create agglomerated phases as the mentioned particles are not effectively influenced by the rotation of stirrer located at the top; the similar problem may appear when the stirrer is located at the top causing turbulence, dissolved gases, as well as non-homogenous distribution of solid phase. At 90° blade

inclination angle, the exchange of material seems to be very limited between the upper and bottom regions and therefore the dispersion quality is not equal throughout the fabricated cast composites; stirring condition was better in 45° and 60° inclinations. Interestingly, the lowest de-cohesion of reinforcing particles and that the advent of unwanted compound like Al_4C_3 have been detected in the fabricated composites when the blade angle has been chosen as the optimum value of 45° (see Figure 5b) [84]. In another research conducted by Hashim et al. [95] and Nagata [90], a depth of ~30% was recommended as an optimum depth for the rotating impellers. Finally, based on a water simulation model, it was estimated that a stirrer having four vertical baffles of 30° blade angle (among 15°, 30°, 45° and 60°) is optimum [85,96]. With smaller angles, the particles may tend to accumulate at the bottom and with larger angles, a radial variation in particle distribution was predicted.

Stirring speeds lower than ~100 rpm and higher than ~600 rpm are not generally recommended [83,87]. At stirring speeds lower than 100 rpm, mixing will not be adequate and hence wetting is not influenced enough; excessive speeds (for example 700 rpm in SiC/Al) usually result in adverse results such as vigorous turbulence, contaminants, gases, and oxide absorbance from the atmosphere and therefore a poor microstructural and mechanical property is expected [87,97]. Under excessive speed conditions, the vortex size (height and width) may become very large due to strong centrifugal forces and hence unbalanced angular flow with vigorously scattered particles towards the crucible walls is most probably anticipated. With optimum speed, however, more particles in longer durations are entrapped and embedded in the metal matrix (see Figure 6) [37].

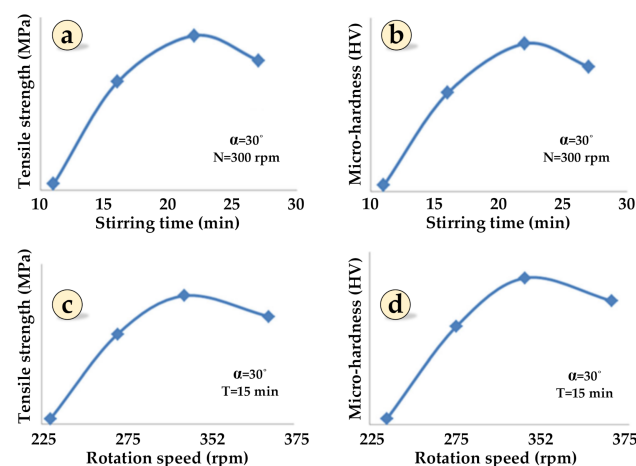


Figure 6. Tensile (a,c) and hardness (b,d) values of TiC/AA6061 composites. α is blade angle, T stirring time, and N stirring speed reproduced from [37], with permission of Springer, 2017.

The process of incorporating particles in a molten metal needs enough time as the shorter time may not provide the desired distribution and too long a stirring time may lead to fluid turbulence leading in turn to more entrapped gases from the atmosphere and higher amounts of voids and porosities. Stirring time is a key factor with an optimum value for a given solid/liquid system [37,38]. It was reported that stirring lower than 5 min in SiC/Al system [52], 15 min in TiC/AA6061 [37] (see Figure 6) is insufficient. It has been found that more stirring time is needed for lower impeller rotation speeds and vice versa; for instance, to obtain uniformly distributed 10% SiC particles in glycerol/water solution, a stirring time of ~39 min with 200 rpm stirring speed is needed while the same particles only require 9 min stirring with the impeller speed of 500 rpm [38]. In addition, the stirring time/speed should be more in higher viscosities; for instance, the stirring times of 0.25 min and 28.3 min are necessary when the particles are dispersed in the viscosities of 1.0 mPas and 300 mPas, respectively [38]. As seen, the optimum stirring time and speed varies based on material type and composition, temperature, reinforcement properties, melt volume and many other processing settings such as impeller geometry, etc. For instance, it has

been found that the effect of temperature/viscosity on the stirring is dominant as the stirring/streamline is more localized around an impeller rotating in a higher viscosity fluid while the situation is better in lower viscosities [95] and that particles may settle in the crucible base if the melt temperature is excessively high.

When the size of particles is reduced, the porosities and voids entrapped within the composite material tend to increase; further, decreasing particle size and increasing weight fraction may reduce the wetting [98] as it seems more intensive shearing force should be applied to disintegrate clusters and to deagglomerate particles with smaller sizes. The problem is even more pronounced when nanosized particles are to be incorporated. Sometimes when nanosized reinforcing particles are added to a melt, mechanical stirring is unable to achieve a well-dispersed and fully de-agglomerated solid reinforcement. In such circumstances, the melt slurry should be treated by other methods like thermal approaches or an additional mechanical agitation, i.e., applying high-intensity ultrasonic irradiation [46,81,99–102].

Smaller particles, especially nanosized reinforcements, have extremely high aspect ratios and hence stronger interparticle forces commonly appear in MMNCs being considered one of the most problematic issues of nanocomposite manufacturing. Nonetheless, nanoparticles usually need more time to settle based on Stoke's Law [38]. Ultrasonication could overcome the inter-particle forces and disperse the particles evenly in a host metal matrix owing to strong shock waves and micro-jets associated with the collapse of cavitation bubbles.

It has been frequently reported that ultrasonic treatment is able to clean the outer surface of reinforcing solids, alter the chemistry of surfaces and reduce the contact angle through changing the particle-melt system from non-wetting to a wetting state. It should be noted that the cleanness of reinforcement surface is of crucial importance as it directly affects the affinity between a given filler material and metal matrix. Ultrasonic treatment, etching by various techniques as well as heating at suitable temperature and atmosphere could provide a clean surface. One of the most important effects of ultrasonic treatment is increasing the surface energy of solid reinforcements in liquid metals. Ultrasonic irradiation greatly promotes mass transfer and diffusion phenomena, sharply decreases the time of wetting and enhances penetration ratio into the layers of solid materials by molten liquids [81,99,101,103]. Zhao et al. [102] reported the wettability and spreading behavior between aluminum and graphite wherein a greatly enhanced wetting condition was realized using ultrasonic agitation for a period of 20 min with 20 kHz vibration frequency and an amplitude of 100 μm . As confirmed by numerical simulations, the wetting angle may decrease substantially from 130° for not having ultrasonication conditions to 15° under the action of ultrasound, as demonstrated in Figure 7 wherein it has been observed that those reaction products may affect the wetting [21,32].

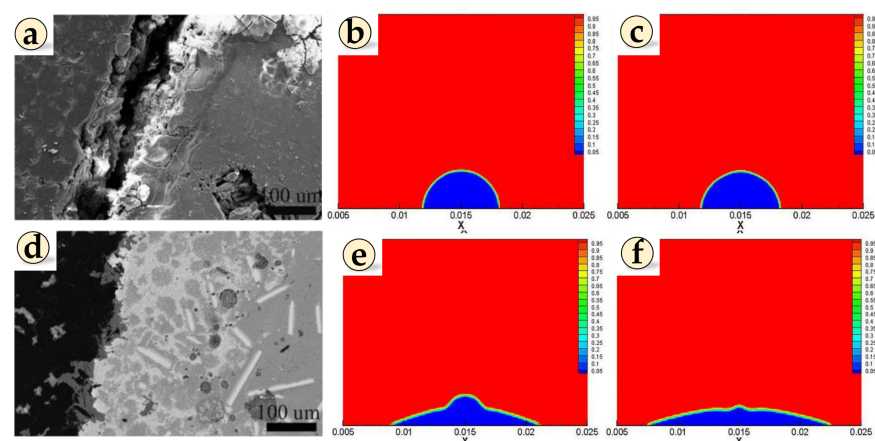


Figure 7. The wetting and spreading effect of ultrasonic irradiation in carbon/aluminum system. (a) the SEM of interface without ultrasonic at the time steps of (b) 900 and (c) 1300 steps. (d) the SEM of interfacial region with ultrasonic at the time steps of (e) 900 and (f) 1300 steps [102].

The two main probable mechanisms of ultrasonic deagglomeration, studied by both computational and experimental efforts, are (i) cavitation (see Figure 8a–c) and (ii) streaming (see Figure 8d) [8]. Transient ultrasonic cavitation (with radii ranging from one to a few hundreds of micrometers) is able to provide an implosive impact being very intensive (ranging from 1–4000 MPa in aluminum) to break up the agglomerated phases and disperse the particles evenly throughout the melt matrix [104,105]. Due to acoustic pressure, acoustic streaming creates a fluid flow in a composite melt being a very influencing factor in well-dispersed well-distributed particles.

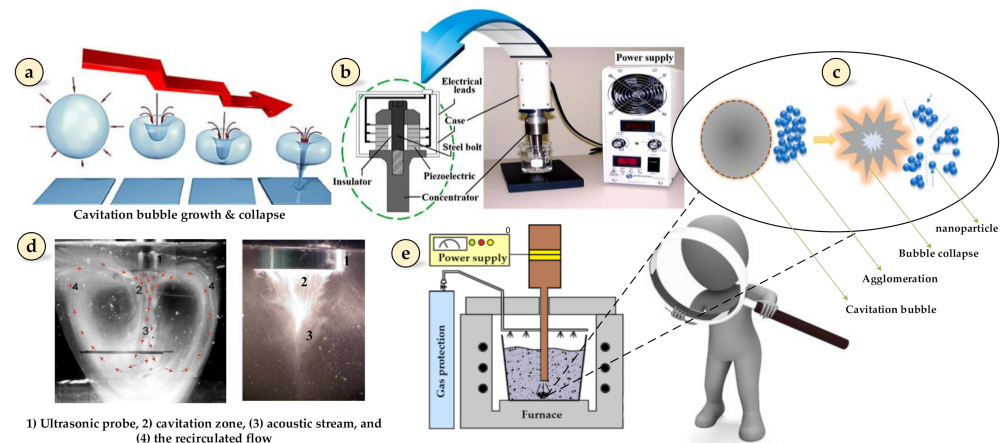


Figure 8. (a) Ultrasonic cavitation bubbles from growth to impulsive collapse, (b) a high-intensity ultrasonic system consisting of a number of piezoelectric rings bolted between a steel backing element and concentrating matching part, (c) upon cavitation collapse near the agglomerated particles, the impact of micro-jets disintegrates the particles, (d) acoustic streaming in a fluid initiating from point 1 to 4, (e) a common ultrasonic assisted melt processing of MMCs/MMNCs under inert gas protection.

As shown in Figure 8e, most of ultrasound-assisted composite manufacturing methods generally consist of a furnace, crucible as well as an ultrasonic apparatus powered by a power supply generating adequate power to be delivered into the melt slurry. Ultrasonic waves, on the one hand, greatly intensify flow convection induced by the cavitation activation, and facilitate the heterogeneous nucleation and growth of solidification sites, hence a significant grain refinement is expected when a proper ultrasonic is employed. On the other hand, the ultrasonic melt treatment may considerably alter the physical and mechanical properties [46,99,106,107]. Inadequate treatment may not have a sufficient deagglomeration effect while excessive flow velocity may induce severe turbulent fluid flow; as a consequent of extreme agitation, those deagglomerated particles could re-agglomerate depending on the local fluid flow patterns.

Many research efforts have compared the physical properties before and after the treatment by ultrasonication based on which a significant grain refinement as well as a reduction in the size of particles (de-agglomeration) homogeneously dispersed in the metal matrix has microstructurally been observed, all indicating the effectiveness of ultrasonic melt treatments. Ultrasonic wetting has already been applied on a variety of metallic composites among which aluminum [104], magnesium alloys [108], and transition metal alloys [109] are usually being considered as matrix; further, a variety of ceramics/oxides/nitrides/carbon allotropes, such as SiC, Al₂O₃, CNTs, etc. are also being utilized as reinforcements.

The required intensity (I) for breaking up an agglomerated phase can be calculated by the following expression [104]:

$$I = 2W_L \left(\frac{\sigma}{D\omega\rho_L} \right)^2 \quad (5)$$

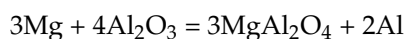
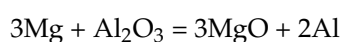
where I is the intensity, σ the tensile strength of the agglomerated reinforcement, W_L the acoustic power, ω the frequency, ρ_L liquid metal density and D the assumed diameter of agglomerated phase. The deagglomeration is greatly dependent on the inter-particle forces, time of treatment, the velocity and impact of ultrasonic microjets as well as the viscosity of composite slurry. The deagglomeration is highly dependent on the interfacial energy between nanoparticles and liquid metals, the duration and the maximum value of the velocity pulse, as well as the size of the nanoparticle agglomerates.

5. Chemical Agent Addition

Wettability of cast metal matrix composites could be greatly influenced by reactive wetting through the addition of alloying elements such as Ti [110,111], Mg [27], Cr [112–114], Ca [115], Sr [116,117], Mn [118], Ce [110], Cu [119,120] and Zr [121] to a melt matrix improving the wettability through decreasing the surface tension and lowering the reinforcement-matrix interfacial energy [30]. The interfacial reactions between the molten metal, alloying elements and reinforcing agent are very complicated; for instance, Cr_{23}C_6 , Cr_3C_2 , Cr_7C_3 , CrSi , $\text{Cr}_5\text{Si}_3\text{C}$, Cr_3Si can be formed when Cr is added to a SiC reinforced aluminum/magnesium composite system [30]. Although, the exact effect of alloying elements has not yet been fully understood [30,107,122], herein a list of alloying elements and their effects on the wetting behaviors are presented:

Magnesium is one of the most important alloying elements in metal matrix composites with a great capacity to increase the solid surface energy, decrease the solid-liquid interfacial energy and reduce the surface tension to a great extent. The presence of Mg scavenges the oxygen at the interface, thinning the gas layers on the solid surface providing better wetting conditions [27]. It has been seen that while Mg, Li and Ti shorten the incorporation time in SiC/Al system, Cu and Zn prolong it [110]. As shown in Figure 9, Mg improves the wetting behavior in SiC reinforced aluminum matrix composites reducing the contact angle from $\sim 92^\circ$ to $\sim 78^\circ$ at 1173 K after 30 min under Ar protection, presumably owing to the deoxidation of aluminum surface, good wettability with SiC oxide films (i.e., SiO_2), and finally the reduction of surface tension.

The interfacial energy is usually decreased by the addition of Mg, facilitating the reactions at the surface of reinforcements [27,83]. It has been realized that 2.0 wt.% Mg is enough for most aluminum-based MMNCs, as higher amounts may lead to unwanted compounds and lower percentages may result in an insufficient alloying effect [27,61,77,123–125]. Mg either on the cast top surface or in the melt could reduce reactive elements and then boost the affinity between reinforcing agent and liquid metal matrix. While the surface tension of Al and Al-Si (11.8 wt.%) are respectively 0.760 Nm^{-1} and 0.817 Nm^{-1} , the addition of 3.0 wt.% Mg may reduce the surface tension of Al to 0.620 Nm^{-1} at 720°C . Sukumaran et al. [125] believed that the addition of Mg to SiC reinforced A356 composite is essential to fabricate the stir-cast composites; the optimum weight fraction has been suggested as ~ 1.0 wt.% below which it may lead to agglomeration while excessive amount may reduce the casting fluidity, increase viscosity, or even produce un-wanted compounds like those low-melting constituents (e.g., Mg_5Al_8) diminishing the final mechanical performance [126]. Mg reacts with the oxygen present on the surface of reinforcements thinning the gas layer and consequently improving the affinity between the reinforcement and its metal host. Mg has a capability to chemically interact with the reinforcing particles (e.g., Al_2O_3) and produce new compounds (e.g., MgAl_2O_4) which is readily wetted. The following reactions are possible in Al-Mg alloys:



MgO is usually created in high magnesium contents of about >1.5 wt.% at lower temperatures while MgAl_2O_4 appeared in the lower weight fractions of <1.5 wt.% [124]. It has been revealed that [77] the addition of Mg could effectively reduce the time and

temperature needed for Al-Al₂O₃ composite to reach an equilibrium state; the pure aluminum needs a temperature above 1050 °C to wet the alumina while the temperature of 900 °C is quite enough for the Al-Mg/Al₂O₃ composite; furthermore, a time period of 20 min is enough to reach an equilibrium wetting condition in case 10 wt.% Mg is added to the melt slurry. Also, a thin spinel layer of MgAl₂O₄ (of 5 µm thick) was observed in the interfacial region contributing to the modification and rupture of oxides, hence providing clean wettable surfaces [77]. According to Contreras et al. [127], an increase in Mg content and temperature results in an improved wettability through the formation of reactive interfacial products namely Al₄C₃, MgAl₂O₄, and MgO.

Ceramic reinforcing materials are usually wetted by the metals by interfacial reactions (i.e., reactive wetting) reducing solid/liquid interfacial energy as well as producing new compounds at the interface [128]. The addition of chemical elements like Mg to a metal matrix can be an effective approach to improve wetting in a variety of reinforcement-matrix systems. For instance, the addition of 7.0% Mg to Al₂O₃ reinforced A356 [129], 2.0 wt.% La to Al₂O₃ reinforced Al [130], 7.0 wt.% Mg to Al₂O₃ reinforced Al [77] could effectively enhance the affinity in MMNCs.

According to Froumin et al. [131], the oxygen entrapped between the TiC and Cu melt strongly inhibits the interfacial interactions leading to non-wetting behavior; it has been found that alloying with aluminum has a pivotal role on decreasing equilibrium contact angle of TiC/Cu-Al system, probably owing to in-situ deoxidization of surface oxides and oxycarbides through Al evaporation, so although Al has been frequently used as matrix element, it has been employed as a chemical agent to improve wettability.

Shao et al. [130] could promote the wetting of Al₂O₃ by molten aluminum through the addition of the rare earth element La (2.0 wt.%) to the composite slurry reducing the surface tension and the contact angle from 90.5 °C in Al-Al₂O₃ to less than 80 °C in Al-La-Al₂O₃ systems. The free energy formation of La₂O₃ is lesser than that of Al₂O₃ and hence, the reduction in wetting angle is expected and supposed to be due to the formation of new La₂O₃ phase at the interface between the reinforcer and the corresponding matrix.

It is believed that the addition of Si up to a threshold of ~12 wt.% to 2014Al-SiC system weakens the formation of Al₄C₃ at 1173 K; above the mentioned threshold, granular Si appeared at the interface deteriorating the interfacial affinity [12,23,26,30,132–134]. Nakae et al. [28,135] added Si to a graphite reinforced aluminum matrix composites and realized three distinct characteristic phases: (i) dynamic non-equilibrium, (ii) quasi-equilibrium, (iii) chemical non-equilibrium and (iv) equilibrium states with increasing adhesive tension due to reactive wetting. Si has a lower surface tension than that of aluminum so it can reduce the surface tension at the interfacial region of aluminum matrix composites; furthermore, SiO₂ has better affinity with Al than that with Si [30,136]. Similar behavior was reported by Laurent et al. [29], Liu et al. [12] and Ferro [134] wherein the Si addition significantly suppresses the formation of unfavorable compound like Al₄C₃, enhanced reactive wetting and clean bonding in interfacial zone, all leading to a better reinforcement-matrix interface. It is noteworthy that when Shen and co-workers [107] studied the polarity effects on the wettability in SiC-reinforced aluminum matrix composites, they observed that the reaction at the Si-terminated surface might be stronger and faster than C-terminated surface.

An et al. [30] studied the effect of alloying elements on the wettability of SiC-Al system and observed that the addition of Si improves but Cu deteriorates the wettability; however, both weakened the formation of harmful Al₄C₃ intermetallics. It has been revealed that Mg had a limited improving effect on the wettability unless SiC is pre-oxidized. Ti addition has also been recognized as a favorable agent owing to the formation of titanium carbides TiC_x in the interface. Figure 9a,b show the variation of contact angle versus time for SiC-Al system having different Si contents. It is demonstrated how the contact angle varies when the different contents of alloying elements are added to the melt (see Figure 9c).

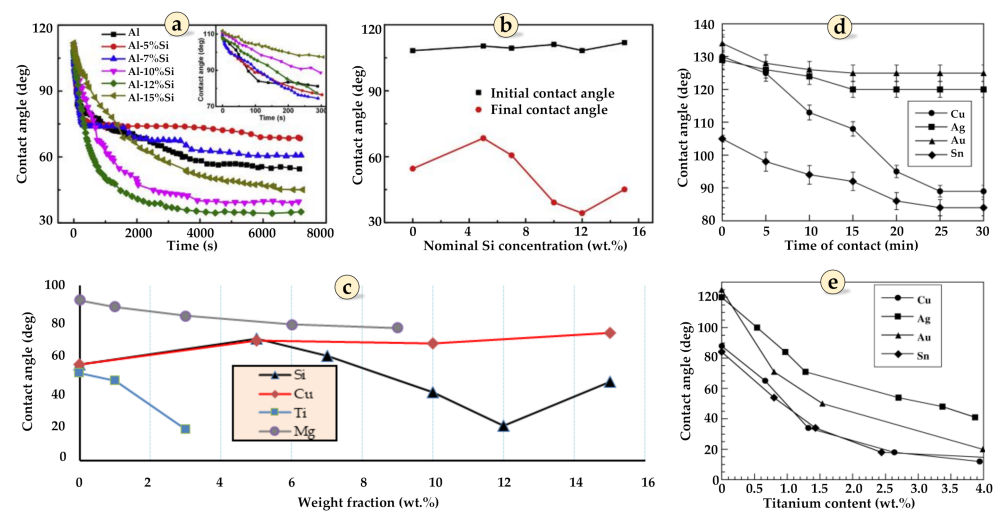


Figure 9. (a) Contact angle in SiC-Al system with different contents of Si alloying element, (b) initial and final (equilibrium) contact angles of SiC/Al reproduced from [30] with permission of Elsevier, 2019. (c) the effect of different alloying elements on the wetting angle of SiC/Al composite. (d) the effect of Ti alloying element on wetting between TiC and (e) different alloys of Cu, Ag, Au and Sn reproduced from [137], with permission of Elsevier, 2005.

Since the enthalpy of mixing Al and Cu is negative (-28 kJ mol^{-1} [29]) providing a relatively potent affinity between these two elements, the activity of Al might be limited due to the addition of Cu to the composite melt. According to Figure 9, the addition of Cu may reduce spreading rate and increase contact angle owing to the alleviation of interfacial reaction products.

Although Ti has a lot of effects on the final microstructure of metallic alloys such as grain refinement in Al MMCs [137,138], it has a limited solubility in aluminum melts (i.e., 1.8 wt.% at 1173 K) and that the addition of Ti to aluminum melt may increase the viscosity strongly affecting the spreading rate [139]. By prolonging time for 2 h, however, it was seen that the contact angle between Al-3.0 wt.% Ti and SiC surface significantly decreases from $\sim 130^\circ$ to $\sim 86^\circ$ at 1073 K and to $\sim 23^\circ$ at 1173 K after 2 h owing to the interfacial reaction $\text{Ti} + \text{SiC} = \text{TiC} + \text{Si}$; the angle promptly reduces to 17° at 1273 K in less than 20 min. From the viewpoint of thermodynamics, the enthalpy of generating Al_4C_3 phase is $-13.7 \text{ kJ}\cdot\text{mol}^{-1}$ while it is $27.9 \text{ kJ}\cdot\text{mol}^{-1}$ for TiC dominating the wetting conditions [140].

Ti can be used as a binder agent in manufacturing ZTA ceramic particles-reinforced high chromium cast iron (HCCI); Zheng et al. [141] could achieve a contact angle of 17.7° in a ZTA/HCCI system resulting in a composite with an enhanced wear resistance and superior mechanical strength. In an effort made by Zhao et al. [138], it has been seen that the addition of Ti significantly refines the microstructure of nano-TiC particles reinforced aluminum matrix nanocomposites owing to the reactive products of TiAl_3 . According to Frage and colleagues [137], Ti addition either added directly as alloying element or dissolved from non-stoichiometric titanium carbides improves the wetting between TiC and Ag, Au, Sn and Cu (see Figure 9d,e).

It has been noted that zirconium boosts the wettability in $\text{Al}_2\text{O}_3/\text{Al}$ composite in terms of reactive wetting. Due to exothermic reaction in the interface between Zr and Al, a great amount of heat is released facilitating the disruption of oxide layers, promoting the formation of ZrAl_3 precipitates in the interfacial region, all leading to the improved wettability of Zr-coated Al_2O_3 reinforced Al matrix composites [142]. Like some other coating elements like Ni, the thickness of coating shell is important factor in enhancing wettability in metal matrix composite; in case of Zr, the affinity between ceramic particles with molten aluminum increased when the thicker coating layer was employed (see Figure 10).

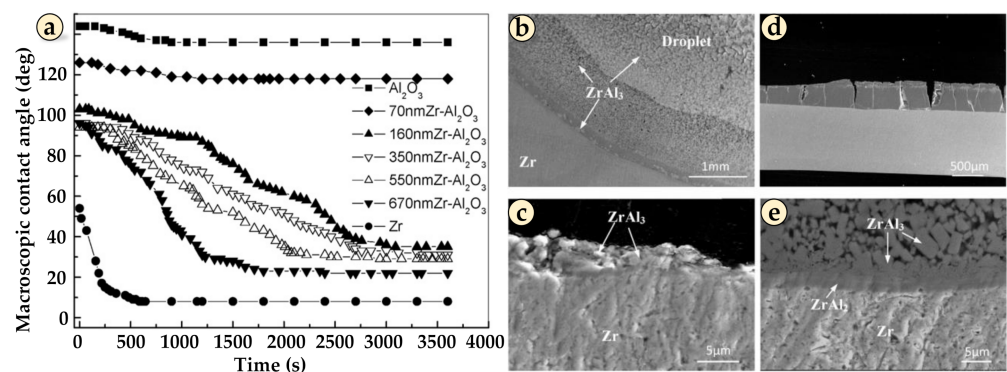


Figure 10. Wettability improvement by Zr coating on Al₂O₃ reinforced Al composite. (a) macroscopic contact angle versus time in isothermal condition at 700 °C, (b) top-view SEM image of solidified sample, (c) cross-sectional view SEM of the interface between precursor and substrate, (d,e) the cross-sectional SEM image taken from the center of the droplet reproduced from [142] with permission of Elsevier, 2016.

Chromium is usually an effective alloying element, for example, in Cu/graphite systems to improve wettability. The contact angle between pure copper and graphite has been measured as about 140° [143] indicating no wetting between graphite particles by the copper matrix, however, the addition of 1.0 wt.% Cr to graphite/Cu composite strongly decreases the wetting angle from 140° to 43° at 1573 K. Molybdenum addition could also effectively enhance the wetting behavior of TiC-Al matrix nanocomposites in terms of enhancing chemical stability of TiC in Al melt, suppressing interfacial reactions, refining the formed Al₃Ti intermetallic, promoting the reaction activation barrier, and improving ductility and mechanical strength [144]. While the abovementioned elements have some advantages and disadvantages, it is strongly believed that still a lot of research efforts should be made to improve the wetting behavior in a given solid-liquid system.

6. Coating

Coating of ceramic particles may increase the overall surface energy of solid phase [22]. Coatings are classified into multilayer and monolayer coatings, either as a diffusion barrier to avoid the reaction between a reinforcer and its matrix, or as a wetting agent to promote the affinity in MMCs or MMNCs. Coating with metals usually changes the chemical composition; however, it is considered as an effective way of achieving better wettability especially when a non-metal reinforcement, like oxides or other ceramics, is incorporated in molten metal matrix [74,145–147]. Sometimes, multi-layer coatings can also be used to reach targeted properties in composite manufacturing [148]. Coating with a metal, like Cu [149], Ni [22], Ag [150], Co [151], Sn [145], Sb [152] or Cr, could be improving wettability as liquid metals usually wet other metals [74]. Chemical or physical vapor depositions, thermal spraying, cementations, electroless and electrolyte methods as well as those sol-gal techniques are the common coating techniques to promote wettability.

Regardless of cost, Ag can be a potential coating layer to prevent the reaction between carbon-based reinforcement with metals like aluminum in composites produced by a liquid infiltration method [150,153]. It has been seen that the wettability between Al and carbon-based fibers being Ag-coated by an electroless plating technique improve due to the formation of an eutectic in Ag and Al, cleaning fiber surface, reducing contaminants and distributing the reinforcing phase homogenously in the matrix material, leading to improved UTS from 79 MPa for the uncoated-carbon fiber reinforced composites to 109 MPa for the coated samples [150]. It has also been indicated that the Ag coating significantly improves wetting characteristics in Ag-coated SiC/Al system wherein Ag sufficiently reduces the interfacial free-energy so the reinforcer is wetted by the melt metal.

Copper is one of the most important coating agents for fabricating high-performance metal matrix composites [149,154,155]. Studying the [151] SiC reinforced aluminum matrix

composites to compare which of Cu, Ni and Co coatings is better for reinforcing purposes, it has been revealed that the Cu coating is the best and Co has the lowest improving effects on mechanical performance, such as ductility, yield strength or hardness. CuAl_2 is one of the main intermetallics in Al-Cu composites with an endothermic nature retaining it near the coated particles making them safe from reaction with melt. According to Maqbool et al. [156], 1.0 wt.% copper coating could be very productive in the fabrication of CNTs reinforced aluminum matrix nanocomposites increasing hardness, yield stress and ultimate tensile stress, respectively by about 103%, 126% and 105% owing to stronger interfacial adhesion with better load transfer provided in the 1.0 wt.% Cu-coated CNT/Al composite. The favorable effect of copper coating was also approved by León et al. [157] wherein electroless Cu coating improved wetting kinetics by reducing the contact angle from 87.3° and 115.2° to 12.6° and 26° , respectively for coated SiC and coated Al_2O_3 after 2 h holding time at 800°C under the protection of argon gas. These reductions were attributed to the significant enthalpy of Al-Cu system producing low melting eutectic compositions and hence increasing the fluidity of melt material with improved spreading behavior. Cu coating delayed the reaction between the ceramic and the aluminum melt as Al_4C_3 phase is created in the interface of uncoated ceramic and aluminum. It has been realized that the reduction rate of contact angle at 800°C in the Cu-coated ceramics ($1.8^\circ/\text{s}$ with the diffusion coefficient of $11.0 \times 10^{-8} \text{ m}^2/\text{s}$) is relatively greater than Ni-coated ceramics ($1.5^\circ/\text{s}$ with the diffusion coefficient of $3.9 \times 10^{-8} \text{ m}^2/\text{s}$) owing mostly to the slower solubility of Ni in Al [22,158].

Ni is a coating material commonly used to improve wettability in metal matrix composites [21,154,159]. Ni is dissolved in aluminum matrix exposing the surface of reinforcing agents (like carbon-based materials) to be directly wetted by melt material without interfacial contaminants, defects or any other dispersoids [160,161]. According to Tekmen et al. [21], Ni is even better coating candidate than Cu in SiC reinforced Al MMCs. 30° at 750°C and 58° at 850°C are the contact angles of Ni-coated SiC with aluminum melt. Ip and co-workers [162] coated graphite particles with Ni to be embedded in aluminum matrix through a CVD method reporting a contact angle of 4° in Ni-coated graphite/Al system at a relatively low temperature of 740°C and under the protection of argon gas, for uncoated graphite/Al, the contact angle was measured as $\sim 140^\circ$. Leon et al. [22,157] reported a small contact angle of 12.2° for Ni-coated SiC/Al system and 11.68° for Ni-coated Al_2O_3 at 800°C owing to high exothermic reactions, extensive heat at the triple points minimizing oxides, an improved mobility of Ni at higher local temperatures, all resulting in improved spreading of the melt on the reinforcement surface. Furthermore, the dissolution of Ni in aluminum melt matrix resulting in the formation of Ni-based intermetallics such as NiAl_3 and Ni_2Al_3 , no dissolution of SiC and no unfavorable precipitation of carbon reaction products such as Al_4C_3 at the interfacial zones are all synergistically contributed to wetting improvements (see Figure 11).

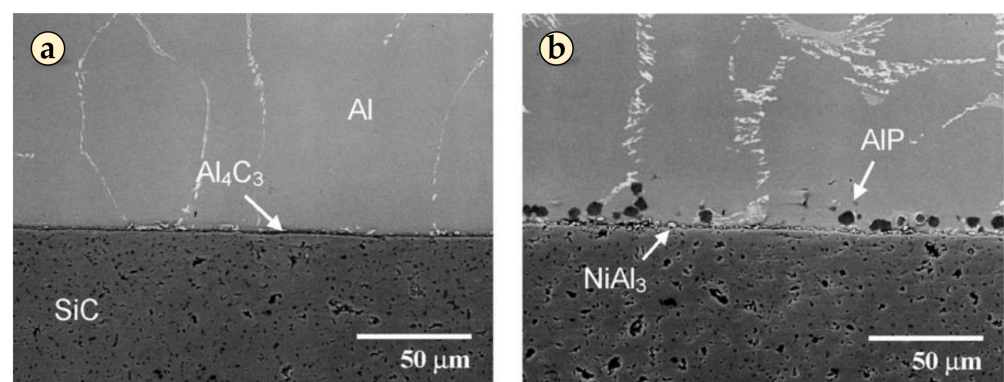


Figure 11. Wettability of aluminum with (a) bare SiC, and (b) Ni-coated SiC, at 800°C reproduced from [22] with permission of 2002.

Coating with nickel has been found to be an effective element to improve the affinity in SiC/Al-Mg alloy system [163]. Coated carbides could be wetted by the aluminum alloy melt at both the temperatures of 650 °C and 850 °C whereas the melt material could wet the uncoated SiC particles at 850 °C, i.e., no wetting at 650 °C was achieved between the uncoated SiC and the melt. Finally, it was reported that nano reinforcing particles coated by nickel could effectively facilitate the de-agglomeration and distribution of SiC nanoparticles in Al-Cu matrix nanocomposites being fabricated via a semi-solid casting route followed by a hot extrusion [164]; Al₃Ni was detected in the interfacial region being the responsible wetting agent. In addition, it has been reported that the coating of alumina particles by Ni could improve mechanical properties, namely impact resistance and fatigue life, owing to good interfacial bonding between the 2.0 wt.% Ni-coated alumina reinforcements and AZ91E matrix [165]. Ru et al. [166] studied high chromium cast iron (HCCI) reinforced by Ni-coated zirconia-toughened alumina (ZTA) particles as the ZTA particles are usually poorly wetted by HCCI. Coating ZTA by a layer of Ni greatly improved wettability and affinity between the reinforcing phase and metallic matrix providing far better interfacial bonding strength and higher mechanical and tribological performance owing to the diffusion of Ni and the refinement of interfacial phases. It has been proved that coating ZTA particles with Ni decreases the wetting angle from 104.1° to 83.6° and 102.3° to 88.2°, respectively when 65Mn steel and HCCI were used as matrix alloy mainly owing to Ni diffusion and reactive product Al₂NiO₄ formed in ZTA/Fe interface [167].

In a study comparing the effect of different coating materials, nano alumina particles were coated by Cu, Ni or Co and used to reinforce cast aluminum matrix nanocomposite wherein 3.0 wt.% Ni-coated Al₂O₃ reinforced composite exhibited higher mechanical properties attributing to better affinity/wettability in interfacial region in terms of lower interfacial defects, reduced surface tension, as well as evenly dispersed and distributed particles throughout the matrix (see Figure 12) [168].

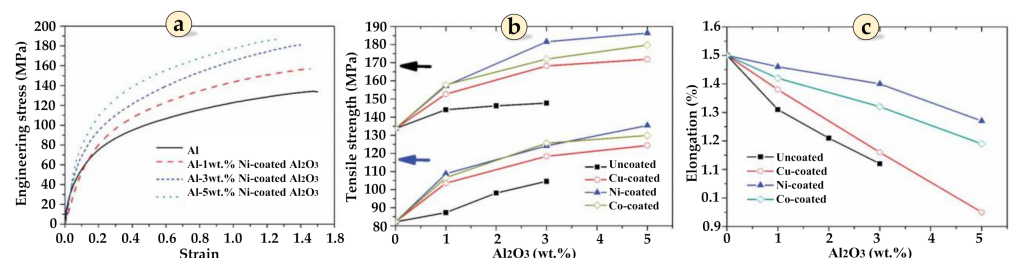


Figure 12. Mechanical properties of aluminum matrix composites strengthened by Al₂O₃ with 3.0 wt.% Ni, Co or Cu coating shells. (a) stress-strain curve; (b) tensile stress and (c) elongation values versus alumina content reproduced from [168] with permission of Taylor & Francis 2018.

Apart from metallic alloying/coating, metal ions have also been used to investigate the wetting behavior between ceramics and metals; some ions have an improving effect while others deteriorate the affinity between reinforcements and host metals. For example, Zhao and colleagues [24] implanted Mo ions on the SiC surface and then used them to reinforce pure Ni and Ni-56Si wherein the contact angle reduces from 27° and 17° to less than 10°, respectively. It was indicated that Ti ion implantation have no noticeable influence on the wetting of SiC/Cu system, probably owing to the surface properties of SiC ceramic [25]. It has been also observed that Pd ion implantation in SiC/Al system may worsen the wetting and increase the contact angle from 30° to 33°, 39° and 42°, respectively, when 5×10^{15} , 5×10^{16} and 5×10^{17} ions/cm² Pd implantation is employed, a behavior that might be attributed to the reduced interactions in the interfacial zones [23].

As said, a number of metals can be coated on reinforcements to be wetted by the melt metal matrices. Instead of metals, ceramics are sometimes considered as coating materials to act as diffusion barriers, for example, in carbon-based materials reinforced aluminum; SiC [169], Al₂O₃ [170], TiB_x [171], TiO₂ [172], and TiB₂ [173] have all been coated on graphite reinforcements in order to avoid the creation of unwanted compound caused by the reactions

between the graphite and Al melt. It has been found that the strength improvement of SiC coated on carbon fibers was more than 189% [169]. Coating of SiC by other ceramics/oxides like SiO₂ [51,174], B₄C [175], Al₂O₃ [176], TiO₂ [51,177], etc. have also been examined to prevent the formation of aluminum carbides and hence to enhance the affinity in SiC/Al system. Also, salts like K₂ZrF₆ [178] have also been coated on carbon-based reinforcements in order avoid the reactions between the fibers and melt aluminum; it has been realized that the contact angle may reduce from ~165° to ~50°, slightly above the Al melting point.

One of the greatest problems in coating reinforcement methods is poor toughness as brittle phases coming to existence by interfacial covalent bonding deteriorating ductility at this region. For example, NiAl₃ with exothermic nature is appeared in Ni-coated carbon or SiC particles reinforced Al MMCs or MMNCs being a wetting promoter; this phase enhances the wetting and improves Yield strength and Young's modulus but greatly degrades the toughness. As mentioned above, the need for metallic bonding at the interface seems to be more effective since they bestow a more ductile characteristic to MMCs or MMNCs.

7. Summary and Research Pitfalls

The need for lightweight high-strength metallic materials is sharply increasing. Metal matrix composites or nanocomposites have many advantages; however, the incorporation of reinforcers of different kinds including ceramics have always been a great challenge as these particles are usually poorly wetted by metal melts. To date, many research efforts have been made to deal with the mentioned bottleneck, all trying to improve wettability in solid-liquid systems; nonetheless, still innumerable questions are still un-answered. In terms of the layout of the current review, first metal matrix composites and nanocomposites are introduced and then the next part deals with the basics and understanding of wetting phenomenon and the main influencing parameters affecting the wettability. In the next section, the effect of thermal processing and the effect of different temperature and time of treatments were briefly discussed based on the current literature. The fourth category is based on mechanical treatments wherein the stir casting by mechanical impellers as well as acoustic-based processes are presented; the effect of impeller design and configurations are introduced and that the main influencing aspects of ultrasonic melt treatment are explained. Apart from thermal and mechanical routes, those methods based on reactive wettings are compactly mentioned wherein an alloying agent e.g., Mg addition to Al composite melt, is added to a composite slurry to enhance the affinity in interfacial region of reinforcer and matrix. Finally, we focus on those strategies wherein a reinforcing agent is coated by a metal or ceramic to prevent melt attack to the strengthening particles.

While extensive studies have been hitherto preformed, still further research efforts are demanded as the current methods have not been successful enough and the problem of poor wetting is yet to be dealt with. Thermal-based techniques remove contaminants, moisture, etc.; however, those thermally treated reinforcements still have poor affinity for the host matrices. Mechanical methods are mainly based on mechanical impellers or ultrasonic treatment wherein the composite slurry is agitated so that the reinforcing particles, especially those with low-density small particles, become engulfed by the melt followed by a rapid solidification. Further, ultrasonic streaming and cavitation are the two key mechanisms for dispersing a reinforcing agent in a metal matrix. Ultrasonic micro-jet caused by cavitation collapse is effectively and efficiently de-agglomerate clusters and any agglomerated phases; however, it is greatly limited to melt volume, melt viscosity and surface tension and that the contamination caused by ultrasonic probe is serious especially in longer melt treatment and higher temperatures. Most importantly, those agglomerated particles tend to rapidly re-agglomerate once the ultrasonic treatment stops demanding a rapid cooling to prevent re-agglomeration. Finally, those alloying and coating techniques have a lot of advantages despite some major drawbacks such as alloying/coating caused brittle intermetallics or changing final chemical compositions, to name but a few.

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