

Article

Fabrication of Al₂O₃/SiC/Al Hybrid Nanocomposites Through Solidification Process for Improved Mechanical Properties

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Abstract: To reduce the cost of nanocomposites and improve the dispersion of nanoparticles, Al₂O₃_{np}/SiC_{np}/Al hybrid nanocomposites are fabricated by combining liquid-state blowing and ultrasonic-assisted casting. The average grain size of the matrix decreases to 39 μm in Al₂O₃_{np}/SiC_{np}/Al, which shows improvements of approximately 118% and 26% as compared to those of Al₂O₃_{np}/Al and SiC_{np}/Al, respectively. X-ray Diffractometer (XRD) results confirm the presence of SiC_{np} and Al₂O₃_{np} in hybrid nanocomposites. The dispersed SiC_{np} and Al₂O₃_{np} are homogeneously distributed in the matrix and no clusters consisting of SiC_{np} and Al₂O₃_{np} exist in the microstructure. Theoretical analyses also verify that there is little possibility for clusters to form in the melt. Good bonding between nanoparticles and Al is demonstrated. Neither cavities nor reaction products exist at the interface. The ductility and the strength of Al₂O₃_{np}/SiC_{np}/Al are improved. The improvement in yield strength of Al₂O₃_{np}/SiC_{np}/Al, in comparison with that of A356, is about 45%.

Keywords: metal-matrix composites; nanoparticles; interface; casting

1. Introduction

One of the great advantages of nanocomposites is their manufacturability. In light of the desired chemical, physical and mechanical properties, the reinforcement and the matrix are selected for nanocomposite preparation. High-strength lightweight nanocomposites become the focus of new material development. Due to the low density, aluminum alloys are applied in many areas, such as automobile and aerospace [1]. Hence, a lot of research is conducted on Al matrix nanocomposites, which have larger ratios of strength to weight than that of aluminum alloys. By reducing the size of the reinforcement from the microscale to the nanoscale, many of detrimental effects of micro-sized reinforcements on composites disappear [2]. For example, compared with the conventional composites, the tensile strength and ductility of nanocomposites are simultaneously improved at both room and elevated temperatures [3]. Good machinability of nanocomposites is also achieved [4]. Nanoparticles result in the enhancement of the hot-tearing resistance of Al–Cu alloy [5]. If the distribution of nanoparticles is uniform throughout the matrix, the increase in strength from the Orowan mechanism can be obtained [6]. However, it is difficult to achieve the uniform distribution of nanoparticles in the matrix. The reasons why nanoparticles tend to form clusters are shown as follows. First, nanoparticles have the poor wettability with the molten Al, which leads to difficult incorporation of nanoparticles into the matrix. Second, the van der Waals forces between nanoparticles are attractive.

A tremendous number of theoretical and experimental investigations have been carried out to disperse these nanoparticles in aqueous solutions [7,8] and polymeric melts [9]. Unlike in

aqueous solutions and polymeric melts, the dispersion of nanoparticles is difficult to be achieved in metal melt. Nanoparticles tend to agglomerate and be sintered in metal melt. It has been proved that mechanical agitation cannot disperse nanoparticles in molten metal effectively [10]. Ultrasound-assisted casting, however, has been reported to offer an extremely promising processing route for the dispersion of nanoparticles [11]. The implosive impact from bubble collapse leads to the dispersion of nanoparticles. Ultrasonic processing was used to disperse nanoparticles in aluminum melt to fabricate $\text{SiC}_{\text{np}}/\text{Al}$ nanocomposites [12]. To improve the incorporation of nanoparticles, the semisolid-state mechanical mixing was used in the high volume fraction of SiC_{np} reinforced Mg–Zn composites [13]. The dispersion of nanoparticles in the melt is related to the contact angle between nanoparticles and the matrix. Nanoparticles with a large contact angle with the matrix is difficult to be incorporated and dispersed in the melt. In addition, friction stir processing [14,15], numerical modeling [16,17] and discontinuous ultrasonic treatment [18] were attempted for enhanced distributions of nanoparticles in material matrix. The interaction between nanoparticles and the solidification front was also investigated [19–21]. SiC_{np} , $\text{Al}_2\text{O}_{3\text{np}}$, AlN_{np} , TiCN_{np} , CNT and graphene are the common reinforcements in Al matrix nanocomposites. Compared to other nanocomposites, SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ have stable chemical properties in molten Al and been widely used as the reinforcement in structural composites. Moreover, SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ of various sizes are easy to be prepared. As the contact angle between $\text{Al}_2\text{O}_{3\text{np}}$ and Al is larger than that between SiC_{np} and Al, it is more challenging to disperse $\text{Al}_2\text{O}_{3\text{np}}$ than to disperse SiC_{np} in the Al melt. However, $\text{Al}_2\text{O}_{3\text{np}}$ is preferred because of its lower price. Through synthetical consideration, both SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ are added into Al as the reinforcement to fabricate hybrid nanocomposites. The dispersion of nanoparticles in metal matrix nanocomposites, which were reinforced with SiC_{np} or $\text{Al}_2\text{O}_{3\text{np}}$, respectively, has been studied. The yield strength (YS) of $\text{SiC}_{\text{np}}/\text{Mg}_2\text{Zn}$ (14 vol.%) is much stronger, providing an enhancement of four times that of Mg_2Zn [3]. $\text{Al}_2\text{O}_{3\text{np}}$ can simultaneously refine the primary silicon and modify the eutectic silicon, leading to an increase in the ductility of $\text{Al}_2\text{O}_{3\text{np}}/\text{Al-20Si-4.5Cu}$ [22]. To date, hybrid composites have attracted increasing interest because they possess the inherent advantages of each component. Nevertheless, the investigations into hybrid nanocomposites, containing two or more kinds of nanoparticles, including the dispersion of nanoparticles and microstructures, are still limited. It has been reported the addition of CNTs significantly improved the dispersion and distribution of TiC nanoparticles in TiC/CNTs/Al nanocomposites fabricated, using a combination of ball-milling and sheath-rolling techniques [23]. It is expected that development of Al matrix nanocomposites by the addition of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ will improve the mechanical properties of the Al matrix, which has not been widely explored.

In this work, hybrid nanocomposites reinforced with SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ were fabricated via combining liquid-state blowing and ultrasonic-assisted casting. The dispersion of nanoparticles in hybrid nanocomposites was characterized by high-resolution transmission electron microscopy (HRTEM). The effects of nanoparticle on the microstructures and mechanical properties of the hybrid nanocomposites were investigated by optical microscope (OM), scanning electron microscope (SEM) and the tensile test.

2. Materials and Methods

Aluminum alloy A356 supplied by Chinalco was used as the matrix material. The chemical composition of A356 is shown in Table 1. The SiC_{np} (an average size of 40 nm) and $\text{Al}_2\text{O}_{3\text{np}}$ (an average size of 20 nm) were purchased from Shanghai Yao Tian Nano Material. SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ were dried in an oven at 423 K for 120 min. A356 alloys were placed in a graphite crucible and then melt in an electric resistance furnace at 973 K. To remove gases and oxides, the aluminum melt was degassed with hexachloroethane for 5 min. SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ with a mass ratio of 1:1 were homogeneously mixed using high-energy ball-milling technology. The mixture was slowly blown into the aluminum melt by high-purity Ar. The ultrasonic processing system was applied to disperse the nanoparticles in the melt. The tip of the ultrasonic probe was placed at a depth of about 30 mm into the melt,

followed by the feeding of the nanoparticles. The processing process of hybrid nanocomposites, including the incorporation and dispersion of nanoparticles in the Al melt, is shown in Figure 1. The ultrasonic processing was carried out at a temperature of 973 K for 15 min. Then, the melt was cast into a cylindrical cast iron mould, of which a diameter and a height are 40 mm and 90 mm, respectively, preheated to 673 K. The melt was under the atmosphere of argon in the whole process. In this experiment, 1.0 wt.% $\text{Al}_2\text{O}_{3\text{np}}$ and 1.0 wt.% SiC_{np} were added into A356 alloys to fabricate $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$. For comparison reasons, samples with the addition of 2.0 wt.% $\text{Al}_2\text{O}_{3\text{np}}$, 2.0 wt.% SiC_{np} and the matrix alloy were also processed.

Table 1. The chemical composition of A356.

Material	Alloy Composition (wt.%)				Impurity Content ($\leq$ wt.%)			
	Al	Mg	Si	Ti	Fe	Mn	Cu	Zn
A356	BAL	0.3–0.45	6.5–7.5	0.08–0.2	0.12	0.05	0.1	0.05

Metallographic specimens were sectioned 51 mm from the bottom of the castings. For microstructural characterization, each specimen was mechanically ground with 180#, 240#, 400#, 600#, 800#, 1000#, 1200#, 1500# emery papers, respectively, and was then polished with diamond suspension (1 μm) to a mirror-like sample surface. Then, each specimen was etched by Keller's reagent (HF 2 mL, HCl 3 mL, HNO_3 5 mL, H_2O 190 mL). To avoid affecting the microstructure, the samples were polished with polishing agents containing micrometers-sized diamonds. An optical microscope (Olympus MPG4, Tokyo, Japan) and a scanning electron microscope (FEI Nova NanoSEM 450, Hillsboro, OR, USA) were used to characterize the morphology and microstructures of the samples. X'Pert PRO X-ray Diffractometer (XRD, PANalytical, Almelo, The Netherlands), of which the scanning speed is $10^\circ/\text{min}$ and the scanning angle range is from 20° to 90° , was used to analyze the phases of the specimens. According to ASTM E112-10, the linear intercept method was used to measure the grain size. A test line was drawn which cut through at least 50 grains in optical images using the software Image-Pro Plus (6.0, Media Cybernetics, Rockville, MD, USA), followed by the count of the intercepts. Counts were made on three blindly selected and widely separated fields to obtain an average for the specimen. The mean lineal intercept length was the size of grains. The interfaces between nanoparticles and matrix and distribution of nanoparticles were investigated with a Tecani F30 G' field emission transmission electron microscope (FEI, Hillsboro, OR, USA). All samples were first cast as tensile bars with a gauge diameter of 5 mm guided by ASTM B108-03a, and were further machined to the specified dimensions with a diameter of 3 mm and a gage length of 15 mm for the tensile test, based on ASTM E8. A tensile testing machine (INSTRON 3382, Canton, OH, USA) with a crosshead speed of 1 mm/min was used to study the tensile properties of the samples. All results were based on the average of three samples.

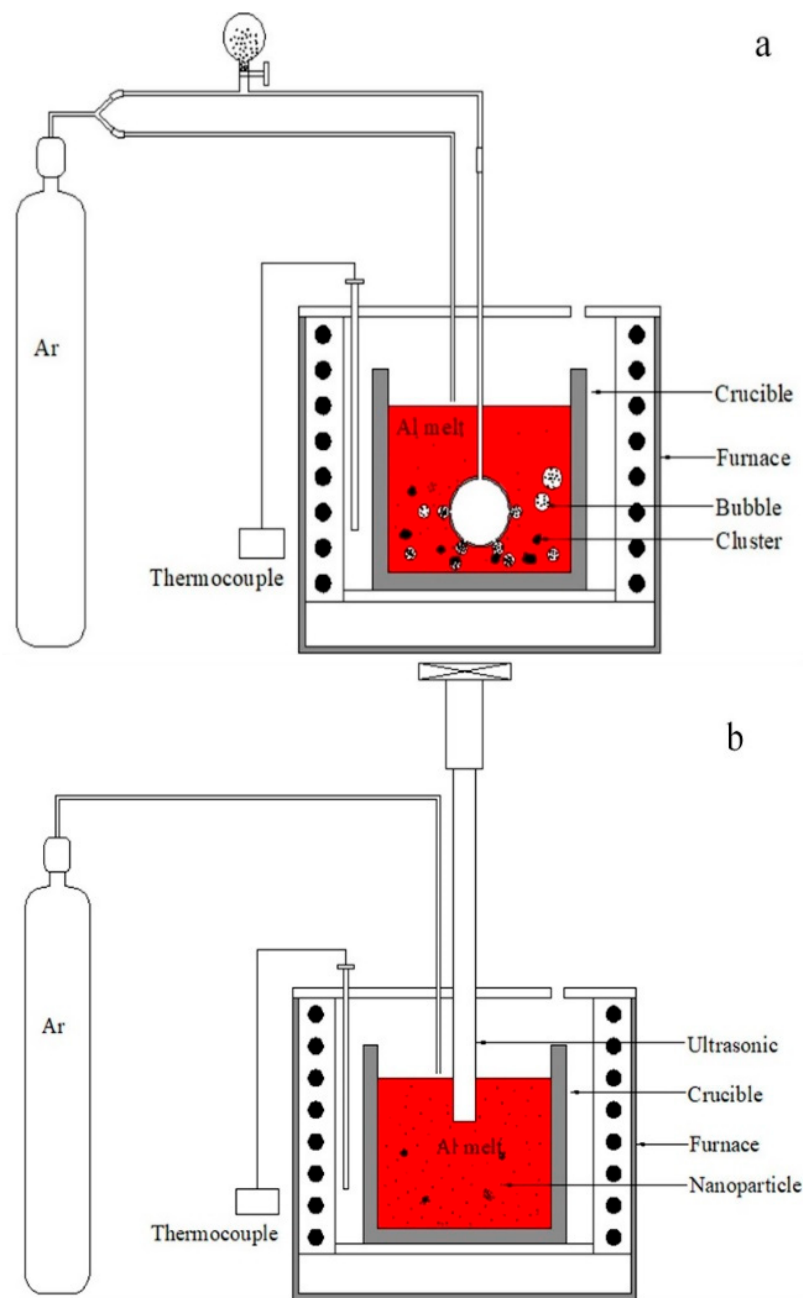


Figure 1. Schematic of the processing method for the incorporation and dispersion of nanoparticles. (a) Nanoparticles are blown into the Al melt by high-purity Ar; (b) nanoparticles are dispersed by an ultrasonic process.

3. Results and Discussion

3.1. Microstructural Characteristics

Figure 2 shows optical microstructures of Al matrix nanocomposites and the matrix alloy. It can be seen that after the addition of nanoparticles into the alloy, the grain size of the matrix decreased. Compared with $\text{SiC}_{\text{np}}/\text{Al}$ and $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$, the grains of the matrix became remarkably smaller, and the number of equiaxed grains in $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ increased. The grain size of the matrix in $\text{SiC}_{\text{np}}/\text{Al}$ was smaller than that in $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$. It was indicated that nanoparticles could significantly affect the grain refinement of the matrix, because nanoparticles restrict the solute diffusion by assembling

onto the interfaces of α -Al, and hence inhibit the grain growth [24]. Therefore, the α -Al growth was restricted with the assembly of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ at the grain boundaries. Furthermore, nanoparticles can act as the sites of heterogeneous nucleation for primary α -Al [25]. Due to the lower crystal growth velocity, a larger undercooling was provided and promoted heterogeneous nucleation. The profoundly increased number of grains resulted in the significant refinement of the grain of the matrix in nanocomposites. Meanwhile, after the addition of different nanoparticles, the grain size of the matrix varied greatly in nanocomposites. The results indicated a strong joint effect of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ on grain refinement of the matrix.

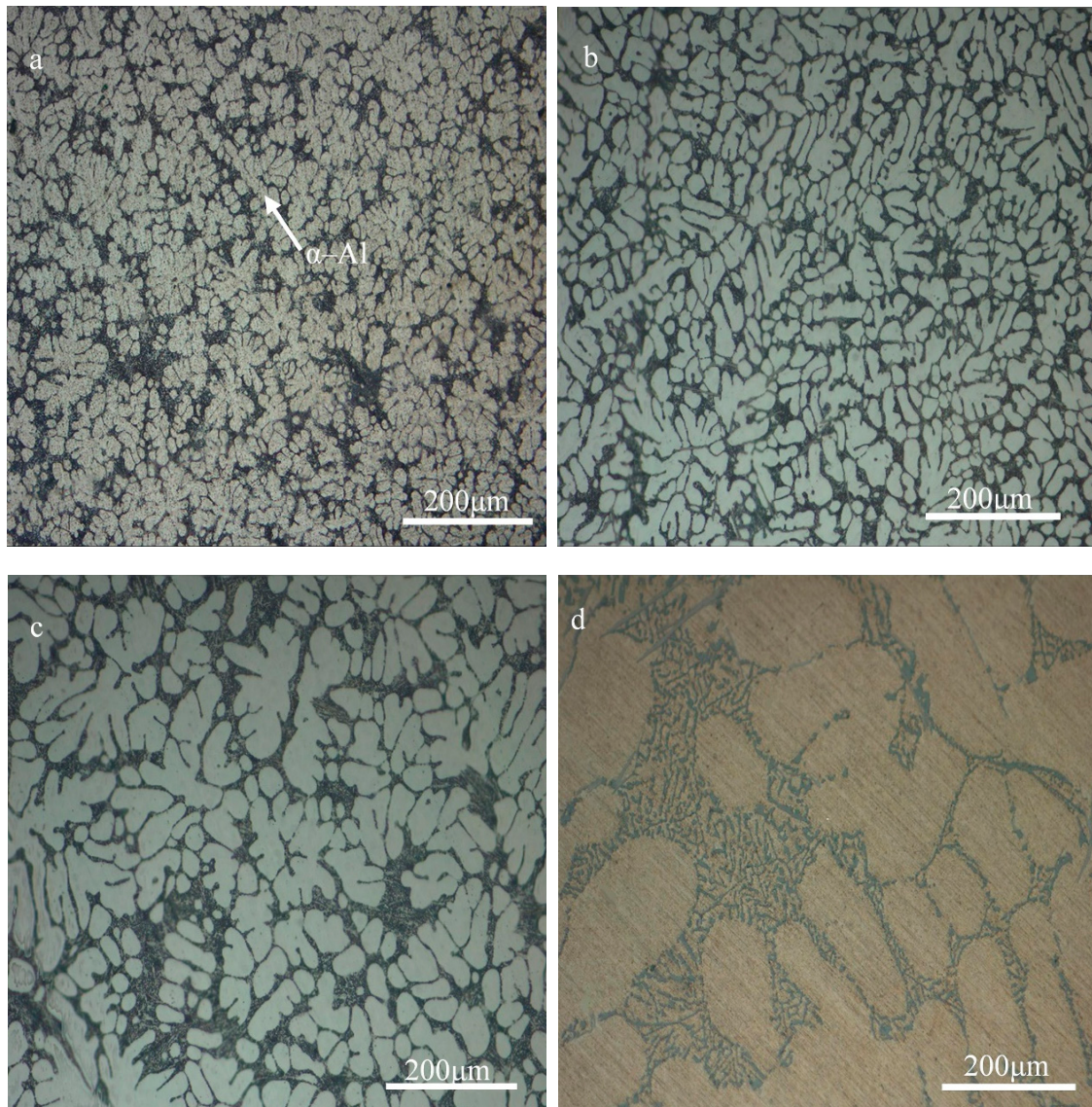


Figure 2. Optical microstructures of Al matrix nanocomposites and the matrix alloy: (a) 2 wt.% $\text{SiC}_{\text{np}}/\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$; (b) 2 wt.% $\text{SiC}_{\text{np}}/\text{Al}$; (c) 2 wt.% $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$; and (d) A356.

The grain size variation with the addition of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ is plotted in Figure 3. The average grain size of the matrix with the joint addition of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ decreased to 39 μm , which showed an approximately 118% and an approximately 26% improvements in grain refinement as compared to $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$ and $\text{SiC}_{\text{np}}/\text{Al}$, respectively. It is further demonstrated that the grain refining effect is most remarkable with the joint addition of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$. It is further demonstrated that the grain refining effect is most remarkable with the joint addition of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$.

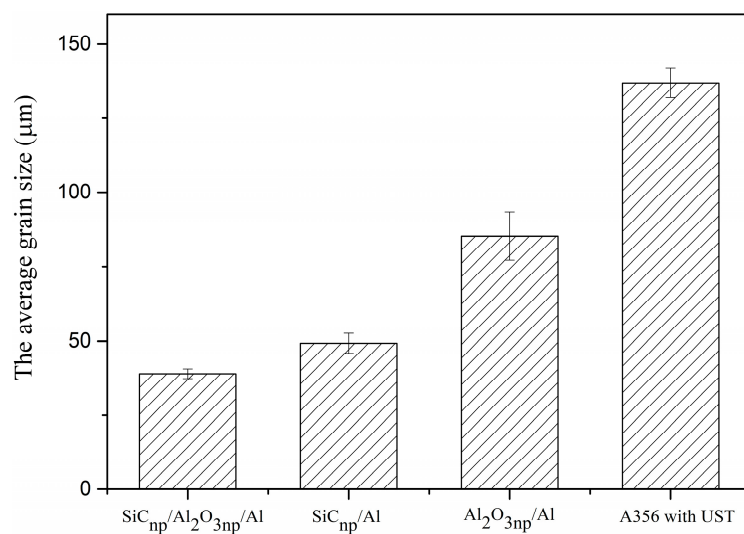


Figure 3. The average grain size of the matrix in nanocomposites and the matrix alloy.

To identify the phases in the nanocomposites, XRD was used to examine the samples. XRD diffraction patterns of the matrix alloy and nanocomposites are shown in Figure 4. As can be seen from Figure 4a, the matrix alloy was comprised of α -Al and eutectic Si phases. After the addition of nanoparticles into the matrix, the diffraction peaks of SiC and Al₂O₃, as well as α -Al and eutectic Si phases, were also identified in Figure 4b. The diffraction results showed that there were the SiC and Al₂O₃ phases in nanocomposites.

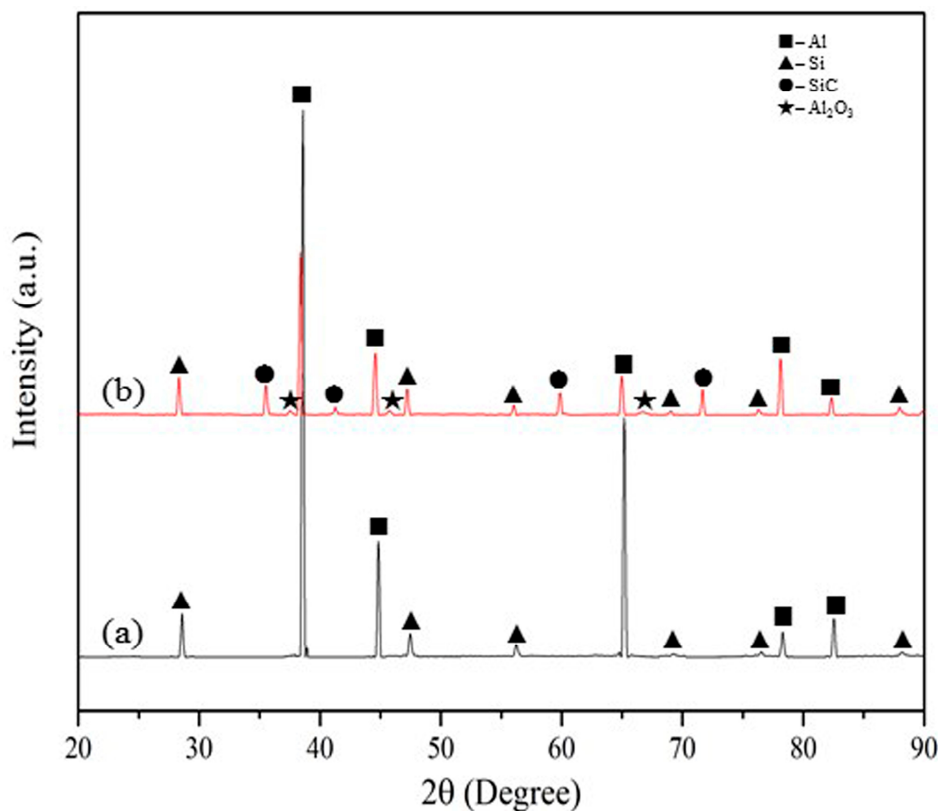


Figure 4. X-ray Diffractometer (XRD) patterns of (a) matrix alloy; (b) 2wt.% Al₂O_{3np}/SiC_{np}/Al composite.

SEM images of the dispersion of nanoparticles in nanocomposites are given in Figure 5. At a magnification of 60,000, the distribution of SiC_{np} , as indicated by white arrows, of which diameters were about 40 nm, was distinguishable in the aluminum matrix in Figure 5a. However, $\text{Al}_2\text{O}_{3\text{np}}$ was vague at this magnification because the size of $\text{Al}_2\text{O}_{3\text{np}}$ was smaller than that of SiC_{np} . The distribution of SiC_{np} was uniform and no large clusters were visible in the matrix, although some small aggregates, which consist of two SiC_{np} , still existed in nanocomposites. At a magnification of 100,000, nanoparticles including SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ were clearly shown, as indicated by white arrows (Figure 5b). The dispersed SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ were homogeneously distributed in the aluminum matrix. From the Figure 5b, clusters consisting of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ were non-existent. It can be seen from Figure 5c, a large cluster consisting of $\text{Al}_2\text{O}_{3\text{np}}$ at a micrometer scale was observed in $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$. From Figure 5d, submicron clusters also appeared in $\text{SiC}_{\text{np}}/\text{Al}$ with some dispersed SiC_{np} around clusters. Furthermore, several pits, which were seen in Figure 5d, resulted from the cavitation of ultrasonic waves. As the formation of clusters reduced the number of effective nanoparticles to inhibit the growth of $\alpha\text{-Al}$, the grain size was coarse in $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$ and $\text{SiC}_{\text{np}}/\text{Al}$.

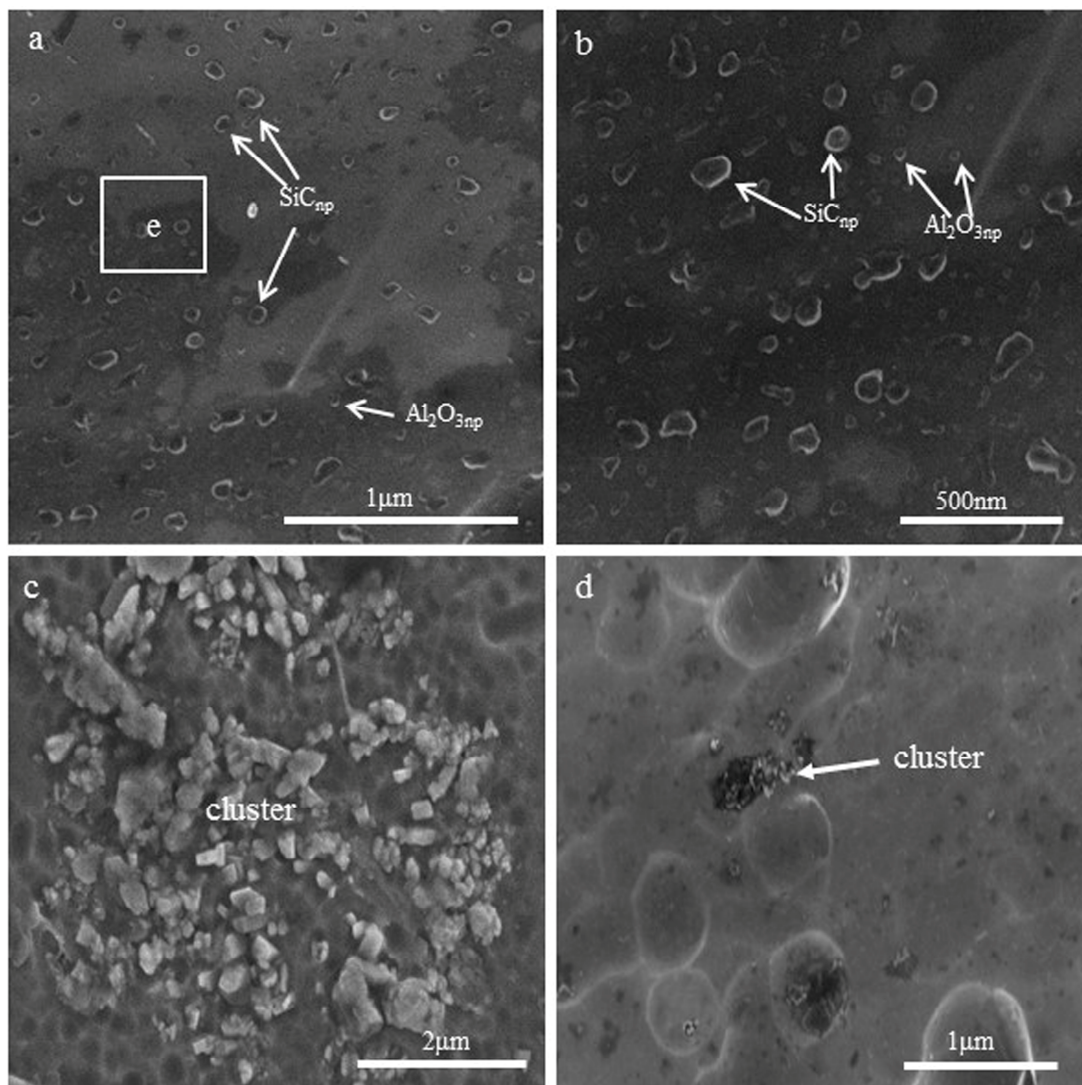


Figure 5. (a) Scanning electron microscope (SEM) image of the distribution of nanoparticles in $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$; (b) magnified image from the area marked as the rectangle e in (a). Large-sized particles are SiC_{np} and small-sized particles are $\text{Al}_2\text{O}_{3\text{np}}$; (c) cluster in $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$; and (d) cluster in $\text{SiC}_{\text{np}}/\text{Al}$. The white arrows indicate clusters.

The dispersion of nanoparticles was decided by the van der Waals forces between the nanoparticles, thermal energy of the nanoparticles, and energy barrier preventing nanoparticle from sintering in the melt. If the energy barrier is not large enough, compared with thermal energy of the nanoparticles, nanoparticles tend to form clusters; if the energy barrier is high and the van der Waals interaction potential is not deep, nanoparticles are self-dispersed in the melt.

For SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ in Al melt at 973 K, the van der Waals interaction potential was calculated by the following equation [26]:

$$w_{\text{vdw}} = -A/(6D) * (R_{\text{SiC}} * R_{\text{Al}_2\text{O}_3}) / (R_{\text{SiC}} + R_{\text{Al}_2\text{O}_3}) \quad (1)$$

$$A \approx \left(\sqrt{A_{\text{SiC}}} - \sqrt{A_{\text{Al}}} \right) \left(\sqrt{A_{\text{Al}_2\text{O}_3}} - \sqrt{A_{\text{Al}}} \right) \quad (2)$$

where A_{SiC} , A_{Al} and $A_{\text{Al}_2\text{O}_3}$ are the Hamaker constants for SiC (248 zJ) [27], molten Al (266 zJ) [28] and Al_2O_3 (140 zJ) [29], respectively; R_{SiC} and $R_{\text{Al}_2\text{O}_3}$ are 20 nm and 10 nm, respectively. The above equation is valid only when two nanoparticles interact through the molten Al for D larger than about two Al atomic layers (i.e., 0.4 nm) [30]. For $D = 0.4$ nm, w_{vdw} is -6.97 zJ.

Interfacial energy barrier [3] was described as following:

$$W(D) = S_{\text{SiC-Al}_2\text{O}_3} (\sigma_{\text{SiC}} + \sigma_{\text{Al}_2\text{O}_3} - \sigma_{\text{SiC-Al melt}} - \sigma_{\text{Al}_2\text{O}_3-\text{Al melt}}) \exp(-(D - D_0)/a_0) (D - a_0)/(D_0 - a_0) \quad (3)$$

for $D_0 < D < a_0$

where σ_{SiC} , $\sigma_{\text{Al}_2\text{O}_3}$, $\sigma_{\text{SiC-Al melt}}$ and $\sigma_{\text{Al}_2\text{O}_3-\text{Al melt}}$ are 1.45 J/m² [30], 1.46, 0.81 and 0.99 J/m², respectively [31].

According to the Langbein approximation, the effective interaction area of two spheres was

$$S_{\text{SiC-Al}_2\text{O}_3} = 2\pi(R_{\text{SiC}} \times R_{\text{Al}_2\text{O}_3}) / (R_{\text{SiC}} + R_{\text{Al}_2\text{O}_3}) D_0 \quad (4)$$

The thermal energy at 973 K was 13.44 zJ, which was higher than $(-w_{\text{vdw}})$. Interfacial energy barrier was calculated as:

$$W_{\text{inter}} = W(D_0) = 1.86 \times 10^4 \text{ zJ} = 1300 \text{ KT} \quad (5)$$

For $\text{Al}_2\text{O}_{3\text{np}}$ in Al melt at 973 K, when D was 0.4 nm, the van der Waals interaction potential was:

$$w_{\text{vdw}} = -41.67 \text{ zJ}$$

This thermal energy at 973 K was 13.44 zJ, which was lower than $(-w_{\text{vdw}})$ of 41.67 zJ. Interfacial energy barrier, W_{inter} , was 11,810 zJ.

For SiC_{np} in Al melt at 973 K, when D was 0.4 nm, the van der Waals interaction potential was:

$$w_{\text{vdw}} = -1.31 \text{ zJ}$$

This thermal energy at 973 K was 13.44 zJ, which was higher than $(-w_{\text{vdw}})$ of 1.31 zJ. Interfacial energy barrier, W_{inter} , was 3.2×10^4 zJ.

By comparing the van der Waals interaction potential and interfacial energy barrier and thermal energy, there was a high possibility for $\text{Al}_2\text{O}_{3\text{np}}$ to form clusters, whereas SiC_{np} tended to be uniformly dispersed in Al melt. For SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ in Al melt, W_{inter} was far larger than the Brownian potential, so it was unlikely for nanoparticles to overcome the energy barrier to reach adhesive contact. Compared with $-w_{\text{vdw}}$, the Brownian potential was much greater. Thus, SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ were allowed to be self-dispersed in the aluminum melt, resulting in no clusters composed of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ existing in the microstructure of hybrid nanocomposites. It should be noted that there were large clusters in $\text{Al}_2\text{O}_{3\text{np}}$ /Al composites.

3.2. The Interface between Nanoparticles and Al

Figure 6 shows TEM images of $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ hybrid nanocomposites. It can be seen from Figure 6a, nanoparticles, indicated as dark spots in the microstructure, were dispersed completely and distributed approximately uniformly in the matrix. No clusters consisting of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ were found in the Al matrix. Complete dispersion and uniform distribution of nanoparticles, indicated by bright spot in Figure 6b, were further confirmed. Figure 6c,d are HRTEM images, showing the interface between a SiC_{np} with an interplanar distance of 0.295 nm and an $\text{Al}_2\text{O}_{3\text{np}}$ with an interplanar distance of 0.232 nm and Al matrix, respectively. The electron diffraction spot of the nanoparticle in Figure 6c was consistent with that of SiC_{np} . Moreover, the electron diffraction spot of the nanoparticle in Figure 6d was the same as that of Al_2O_3 . It was demonstrated that the interface between the matrix and the reinforcement plays an important part in nanocomposites. The interface formed between nanoparticles and the aluminum matrix did not reveal the presence of reaction products. In addition, no interface debonding or cracks were observed, verifying outstanding interfacial bonding between nanoparticles and Al.

The probable reaction between the molten Al and SiC at 973K was shown as follows [32]:



According to XRD results and HRTEM images between SiC_{np} and Al, reaction products were not detected, which can be explained as following. First, the formation of Al_4C_3 was restricted by the quantity of Si. Second, due to the short time, the amount of generated Al_4C_3 after short reaction time was small. In addition, the amount of free carbon on the surface of nanoparticles was small. Since Al_4C_3 is the brittle compound and can react with cold water, the formation of Al_4C_3 damages the interface between Al and SiC_{np} . Hence, reduced interfacial reaction contributed to improvement of the composite performance.

3.3. The Interaction between Nanoparticles with Solid–Liquid Interface

The distribution of nanoparticles during the solidification has the significant influence on the microstructures of nanocomposites. The investigations into the interaction between the particle and the solid–liquid interface have been extensively conducted. According to the critical velocity model, which only considers repulsive and drag forces, nanoparticles are almost pushed to the grain boundaries. However, some nanoparticles distribute homogeneously in the grain [33]. Hence, the previous models are not valid. The critical solidification velocity model for pushing of nanoparticles considering Brownian motion is described as follows [34]:

$$V_c = \frac{1}{6} \frac{A}{\eta h^2} \left(1 + e^{\pi^2(1 - \frac{r}{r^*})} \right)^{-1} \quad (9)$$

$$r^* = \left(\frac{27}{4} \frac{k_B T \eta}{\pi (\rho_p - \rho_L)^2 g^2} \right)^{\frac{1}{5}} \quad (10)$$

where A is Hamake constants, r is the radius of nanoparticles, ρ_p is the density of nanoparticles, ρ_L is the density of the alloy melt, η is the viscosity of the alloy melt, h is the equilibrium separation distance (1×10^{-8} m) and g is the gravitational acceleration (9.8 m/s^2). According to the parameter values, shown in Table 2, the critical radius of $\text{Al}_2\text{O}_{3\text{np}}$ and SiC_{np} are 780 nm and 1000 nm, respectively. If the radius of $\text{Al}_2\text{O}_{3\text{np}}$ and SiC_{np} are 10 nm and 20 nm, respectively, the critical velocity of $\text{Al}_2\text{O}_{3\text{np}}$ and

SiC_{np} are $0.85 \mu\text{m/s}$ and $0.1 \mu\text{m/s}$, respectively. Hence, $\text{Al}_2\text{O}_{3\text{np}}$ and SiC_{np} tend to be engulfed by the solidification front.

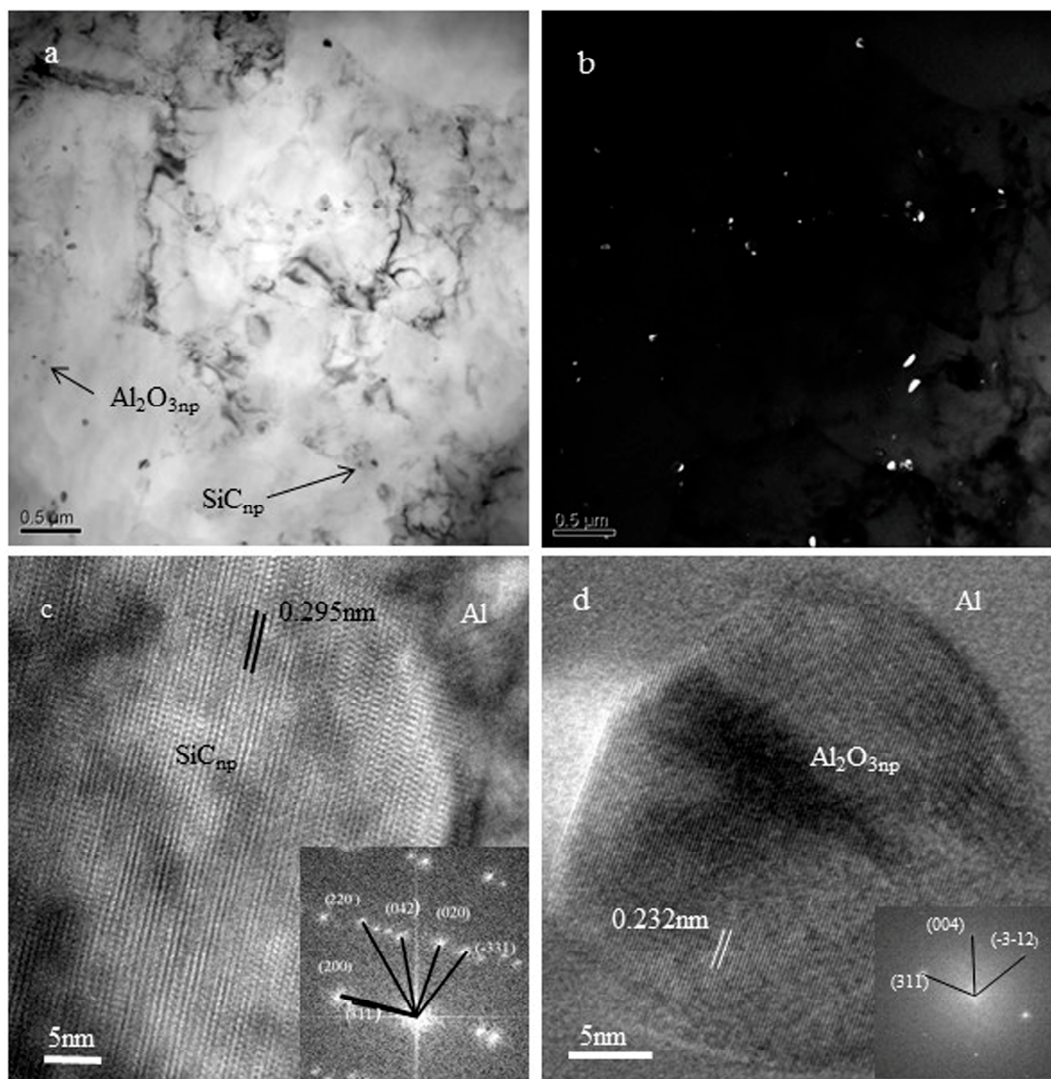


Figure 6. (a) Transmission electron microscopy (TEM) bright-field image and (b) TEM dark-field image of the dispersion of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ in $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$. (c,d) are high-resolution transmission electron microscopy (HRTEM) images of the interface between SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ and Al in $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$, respectively. The insets in (c,d) are the fast Fourier transformation (FFT) of nanoparticles.

Table 2. Parameters used for calculations of critical velocity in $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ alloy [21,34].

Parameter	Value	Unit
η	1×10^{-3}	$\text{Pa} \cdot \text{s}$
K_B	1.38×10^{-23}	J/K
T	973	K
$\rho_{\text{Al}_2\text{O}_3}$	3.7	g/cm^3
ρ_{SiC}	3.22	g/cm^3
ρ_{Al}	2.7	g/cm^3
$A_{\text{solid-liquid-Al}_2\text{O}_3}$	-8.68	zJ
$A_{\text{solid-liquid-SiC}}$	-1.09	zJ
g	9.8	m/s^2

3.4. Mechanical Properties

Comparisons between the YS, the ultimate tensile strength (UTS) and elongation of samples are shown in Figure 7. As can be seen, the YS and UTS of $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ were the largest among these samples. The improvement in UTS of $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$, in comparison with that of $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$, $\text{SiC}_{\text{np}}/\text{Al}$ and A356, were about 40%, 25% and 48%, respectively. The YS of $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ was 215 MPa, increased by approximately 36%, 22% and 45%, as compared to that of $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$, $\text{SiC}_{\text{np}}/\text{Al}$ and A356, respectively. Compared with $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$, $\text{SiC}_{\text{np}}/\text{Al}$ and A356, the increases in the elongation of $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ were 65%, 40% and 51%, respectively.

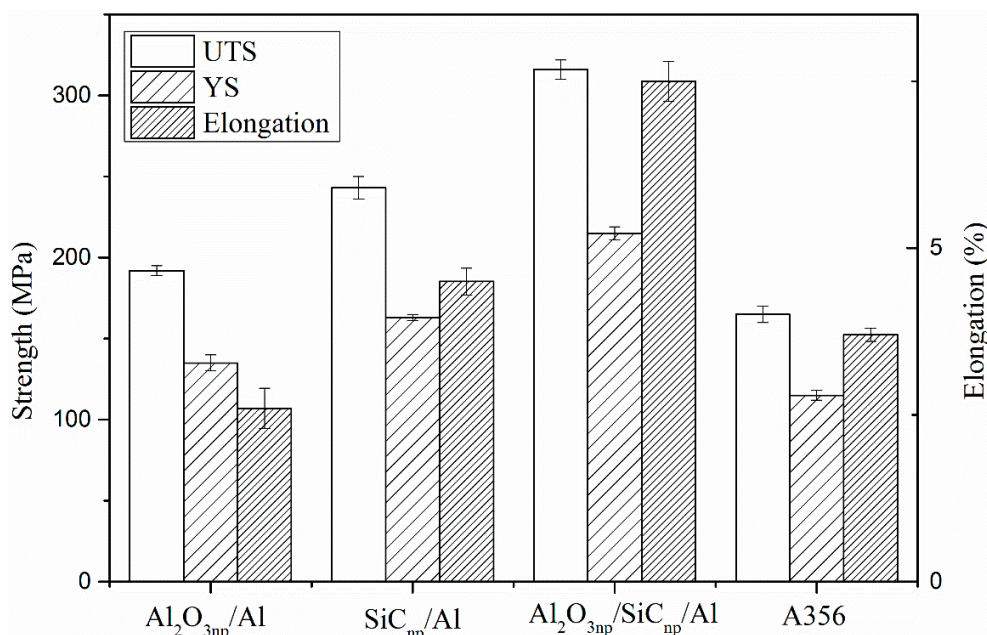


Figure 7. The strength and elongation of nanocomposites and the matrix alloy.

The improvement in strength of the materials usually depends on the cost of ductility. However, the significant improvement of the strength properties was combined with the ductility in $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ hybrid nanocomposites. The strengthening mechanisms, including the Orowan strengthening, generation of geometrically necessary dislocations due to CTE mismatch, the load bearing effect and the Hall–Petch mechanism, contribute to the increase in strength of metal matrix nanocomposites [35]. As small nanoparticles lack the ability to generate adequate strain, the strengthening from the increased dislocation can be neglected [3]. Thus, only three strengthening mechanisms played roles in increasing the YS in Al matrix nanocomposites.

The contribution from the Hall–Petch effect was calculated by the following equation:

$$\Delta\sigma_y = k \left(d_c^{-\frac{1}{2}} - d_m^{-\frac{1}{2}} \right) \quad (11)$$

where d_c and d_m are the grain sizes of nanocomposites and the matrix alloy, respectively, and k is a constant. Loucif et al. investigated the Hall–Petch relationship in aluminum alloys. The value k for the Al alloy at room temperature is $0.326 \text{ MPa} \cdot \text{m}^{\frac{1}{2}}$ [36]. Due to the grain refinement in $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$, the calculated $\Delta\sigma_y$ in the YS of $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ was 24 MPa.

The increased YS from the Orowan strengthening mechanism induced by dispersed nanoparticles was calculated by the following equation [37]:

$$\Delta\sigma_{\text{Orowan}} = \frac{0.13G_m b}{\lambda} \ln \frac{d_p}{2b} \quad (12)$$

where d_p , λ , b and G_m are the size of the nanoparticles, the interparticle spacing, the Burgers vector and the shear modulus of the matrix, respectively. In this study, we calculated the value for $\Delta\sigma_{\text{Orowan}} = 90$ MPa for $G_m = 2.54 \times 10^4$ Pa and $b = 0.3$ nm.

Nanoparticles lead to a large particle-matrix interface even if the volume fraction of nanoparticles is low in nanocomposites. Therefore, the load bearing effect was taken into account. The improvement in strength resulting from the load bearing was calculated by the following equation [38]:

$$\Delta\sigma_{\text{load}} = 1.5v_p\sigma_i \quad (13)$$

where σ_i is the interfacial bonding strength and v_p is the volume fraction of nanoparticles. The calculated $\Delta\sigma_{\text{load}}$ was 21 MPa.

In order to estimate the YS of $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ (σ_{ys}), the Hall–Petch effect, the Orowan strengthening mechanism and the load bearing effect should be incorporated. Sanaty-Zadeh proposed a modified Clyne model, which is more accurate than other methods [39]:

$$\Delta\sigma = \sqrt{\Delta\sigma_y^2 + \Delta\sigma_{\text{Orowan}}^2 + \Delta\sigma_{\text{load}}^2} \quad (14)$$

$$\sigma_{ys} = \sigma_{ym} + \Delta\sigma \quad (15)$$

The theoretical YS of $\text{SiC}_{\text{np}}/\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$, σ_{ys} , was 210 MPa, which was in agreement with the experimental value of 215 MPa. Orowan strength mechanism originating from the uniformly distributed nanoparticles can hinder the motion of dislocations. From the tensile properties, three strength mechanisms were all activated in hybrid nanocomposites, confirming the uniform distribution of nanoparticles.

It was found that the YS of $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$ was about equal to that of A356. The main reason why the YS of $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$ was not improved is the large clusters in $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$ seriously impaired the mechanical properties of $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$ nanocomposites. In the meantime, the clusters changed the interparticle spacing and distribution of nanoparticles in nanocomposites. Due to the negative correlation between the Orowan strengthening mechanism and the interparticle spacing, Orowan strengthening mechanism was not completely activated to significantly improve the strength of $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$ nanocomposites. The sizes of clusters were smaller in $\text{SiC}_{\text{np}}/\text{Al}$ than those in $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$. Therefore, these clusters could be seen as large nanoparticles, making the effect of Brown Motion on small nanoparticles significant [19,20]. However, these large nanoparticles tend to be pushed to the grain boundaries and phase interfaces by the solidification front [40]. Moreover, this imperfect distribution caused deterioration in the mechanical properties of nanocomposites, which could be greatly improved by the decreased number of clusters.

The elongation is an index describing the plasticity of materials. Compared to that of $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$ and $\text{SiC}_{\text{np}}/\text{Al}$, the average grain size of $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ was smallest. Furthermore, the elongation of $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ was found to be largest. The results indicated that $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ had good ductility and plasticity. The fine grains blocked the dislocation motion in the alloy; therefore, its strengthening improved and prevented the origin and propagation of cracks, resulting in the improvement in ductility. Compared with that of other Al matrix nanocomposites in literature [41,42], the UTS and elongation of $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$ was greatly improved.

4. Conclusions

SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ reinforced Al matrix hybrid nanocomposites were obtained. Compared with $\text{SiC}_{\text{np}}/\text{Al}$ and $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$, the grain refinement of the matrix was most remarkable. XRD results verified the presence of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ in hybrid nanocomposites. SEM images indicated that the distribution of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ was homogeneous and no clusters, which consisted of SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$, existed in $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$. TEM images further confirmed that nanoparticles were completely dispersed and uniformly distributed in the matrix. It has been found the bonding between

nanoparticles and Al was very strong. Theoretical studies also showed that it was unlikely for SiC_{np} and $\text{Al}_2\text{O}_{3\text{np}}$ to form agglomerations in the Al melt. Compared with $\text{Al}_2\text{O}_{3\text{np}}/\text{Al}$ and $\text{SiC}_{\text{np}}/\text{Al}$, the strength combined with the elongation was significantly improved in $\text{Al}_2\text{O}_{3\text{np}}/\text{SiC}_{\text{np}}/\text{Al}$.

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