Effect of Nanoparticle Content on the Microstructural and Mechanical Properties of Forged and Heat-Treated TiC/2219 Nanocomposites

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Abstract: In this study, castings of TiC nanoparticle reinforced 2219 aluminum matrix composites with different TiC nanoparticle contents (0, 0.5, 0.9, 1.3, and 1.7 wt.%) prepared using an ultrasound-assisted stirring technology were deformed by multidirectional forging at 510 °C followed by T6 aging treatment. The microstructural evolution and mechanical properties of the 2219 alloy and its composites were investigated and compared. Optical microscopy and scanning electron microscopy revealed that the composite with 0.9 wt.% TiC nanoparticle content possessed finer grains and the lowest amount of Al2Cu phases. The electron backscattered diffraction (EBSD) was used to characterize the sub-grains. The precipitation microstructures of the 2219 alloy and composites with different nanoparticle contents were characterized by differential scanning calorimetry and transmission electron microscopy. It was found that 0.9 wt.% TiC/2219 nanocomposites contained the highest amount of θ” and θ’ phases with shorter lengths. This might imply that the nanoparticles uniformly dispersed in the matrix could facilitate the precipitation of θ” and θ’ phases during aging. Thus, the 0.9 wt.% TiC/2219 nanocomposite showed the best mechanical properties. The ultimate tensile strength, yield strength, and elongation of the 0.9 wt.% TiC/2219 nanocomposite increased by 24.2, 46.1, and 37.2%, respectively, compared to those of the 2219 alloy.

Keywords: aluminum matrix nanocomposite; forging; heat treatment; precipitation phase; mechanical properties

1. Introduction

Aluminum matrix composites are a type of advanced materials, which have advantages that traditional materials do not have, such as their light weight, high specific strength, high specific modulus, low coefficient of thermal expansion, and good wear resistance [1–4]. 2219Al-Cu alloys are particularly attractive materials for aerospace and automotive applications owing to their low density and high strength, where the strength to weight ratio is a major design consideration. Titanium carbide (TiC) nanoparticles have excellent chemical and physical properties such as high chemical, thermal stability, abrasion resistance, creep resistance, low density, and low coefficient of thermal expansion. They are often used as the discontinuous particle reinforcement phase [5,6]. However, composite castings do not meet the requirements of industrial applications, requiring the workpieces to be deformed. After the deformation process, the performance of workpieces is greatly improved. There are many kinds of deformation processes for as-cast workpieces, such as forging, cold rolling, and extrusion. Some researchers have studied the effects of cold rolling and extrusion on the structure and mechanical properties of the composites [7–12]. Compared with cold rolling and extrusion.
processes, forging is an ancient and important method of metal forming. It offers many advantages such as superior mechanical properties, and near net shape production with negligible material wastage. Moreover, the application of forging is not limited by the initial shape of the castings. Forged workpieces not only have high strength and good grain orientation but can meet the industrial requirements without additional processing, thus greatly saving materials [13].

Some researchers have studied the influence of forging on the properties and microstructure of composites reinforced by different kinds of particles. However, most of these composites were reinforced by micro-particles. Ismail et al. [14] showed that the yield strength and tensile strength of SiCp (15–30 µm) reinforced aluminum composites improved by 100% and 40%, respectively, after forging. Moreover, the yield strength and tensile strength of the composites increased with the increasing volume fraction of SiCp up to 17 vol.% and then decreased with further addition of reinforcement. Bharathesh et al. [15] reported that the microhardness and tensile strength of a hot-forged Al-8 wt.% TiO₂ (20–60 µm) composite were higher than those of the matrix material, whereas the ductility was lower. Ceschini et al. [16] investigated the effect of hot forging on the microstructure and tensile properties of AA2618 aluminum alloys reinforced with 20 vol.% Al₂O₃ (20 µm) at room temperature. The hardness, tensile strength, elastic modulus, and tensile elongation of the forged samples increased. Narayana Murty et al. [17] optimized the hot working process condition for 6061Al-SiC and 6061Al-Al₂O₃ and identified the stable and unstable regions in the processing maps from the present instability condition. Other researchers have studied the forgings of different particle reinforced composites prepared by different methods. The forging process can break some of the agglomerated particles, thus facilitating uniform distribution of particles in the matrix and improving the properties of the material [18–20]. However, nanocomposites, especially the forged and heat-treated composites reinforced by TiC nanoparticle (40–80 nm), were rarely studied. Few papers have studied the effect of TiC nanoparticle on precipitation of θ” and θ’ phases to explain the improvement of properties of TiC/2219 alloy nanocomposites.

This study investigated the effects of TiC nanoparticle content on the microstructure and mechanical properties of TiC/2219 nanocomposites. We focused on the impact of TiC nanoparticle content on the precipitation of θ” and θ’ phases and further explained why the properties of composites were improved. The as-cast 2219 alloy and composites with different nanoparticle contents were prepared by ultrasonic-assisted stirring and then forged by the same forging process followed by the same T6 heat treatment. Finally, the microstructures and mechanical properties of the 2219 alloy and its composites were studied. The effect of different nanoparticle contents on the microstructural and mechanical properties was analyzed and discussed from the viewpoint of θ” and θ’ phase precipitation.

2. Materials and Methods

In this study, the 2219Al alloy with a nominal chemical composition of Al-5.8% Cu-0.2% Mn-0.1% Zr-0.05% V-0.35% Fe-0.2% Si-0.02% Mg-0.1% Zn (wt.%) was selected as the matrix alloy, and the TiC nanoparticles (purity: 99.99%, hexahedron shape, diameter 20–100 nm, ShangHai NaiOu Company, Shanghai, China) were used as the reinforcements as shown in Figure 1. The TiC/2219 nanocomposite was prepared by an ultrasound-assisted stirring technology that could promote the wetting of particles and melt, which could facilitate the incorporation of the nanoparticles into the melt. Ultrasonic melt treatment was exerted through a sonotrode that was driven by a high power ultrasonic generator (input frequency, 20 kHz; input power 2.5 kW). The output power and current were 400 W and 6 A, respectively. Sonotrode, made of Ti alloy [21,22], was immersed at a position of 30 mm below the melt surface and vibrated for 15 min in 700 °C. The microstructures and properties of composite castings had been studied in the author’s previous work [23].
TiC/2219 nanocomposite samples with different nanoparticle contents (0, 0.5, 0.9, 1.3, and 1.7 wt.%) were severely deformed by multidirectional forging at 510 °C with a compression speed of 10 mm/s using a 40 MN numerically-controlled hydraulic press [24]. The mold temperature for forging was 460 °C. These five as-cast billets were cut into 80 × 80 × 90 mm³ cuboids. A coating was applied on their surfaces with a brush to prevent the sample from sticking to the mold. Then, the samples were heated to 540 °C in a furnace for 2 h. In each upset forging, the specimens were compressed along different axes with 50% height reduction, and then cooling at room temperature. Figure 2 shows a schematic diagram of the forging process. Five forging processes were applied, wherein the force used for the first to the fourth forging processes was F1, and that for the last forging process was F2 to reduce the deformation rate achieving a relatively large size. The forged samples were subjected to T6 heat treatment, involving solution treatment at 530 °C for 2 h, water quenching, and ageing at 163 °C for 30 h, and cooling at room temperature. The forged and heat-treated samples were used to analyze the microstructure and mechanical properties.

The forged and heat-treated 2219 alloy and composite samples were further used to study the effect of the nanoparticles on the precipitation phase. Specimens were extracted from the middle region in the same axial direction of these 5 samples. Optical microscopy (OM; DSX50240, OLYMPUS, Beijing, China) was performed to observe the grain size. These samples were mechanically ground,
polished, and etched using the Keller solution for OM. Scanning electron microscopy (SEM; JSM-7600F, JEOL, Shanghai, China) was performed to observe the Al\textsubscript{2}Cu phases in the multidirectional-forged heat-treated matrix. Specimens for SEM were prepared by mechanical grinding and polishing. Electron Backscatter Diffraction (EBSD) was used to investigate the sub-grain. The samples of EBSD were ground and then electro-polished in a solution of 30% nitric acid and 70% methanol at 18 V for 50 s. HKL Channel 5 software was used to analyze the EBSD data. Transmission electron microscopy (TEM; JEM2100, JEOL, Hillsboro, OR, USA) was conducted to determine the effect of nanoparticles on the precipitation phases. TEM specimens were prepared by slicing the samples to 0.5 mm thickness and then grinding to 50 \( \mu \)m thickness. After grinding, the slices were punched into 3 mm diameter disks and then thinned by an ion beam to about 5 \( \mu \)m. Differential scanning calorimetry (DSC; Perkin-Elmer 8000, Beijing, China) was performed to determine the role of the nanoparticles on the precipitation kinetics of the strengthening phases. The DSC samples were polished with 400 W metallographic sandpaper to a thickness of 1 mm. Then, 15 mg of slices were removed with scissors and loaded on the DSC system. Experiments were performed at a constant heating rate of 10 \( ^{\circ} \)C/min under a protective atmosphere of pure nitrogen. Room-temperature tensile strength, yield strength, and elongation of forged and heat-treated 2219 alloy, and nanocomposite specimens were determined using a tensile tester (AG-IC100KN, Shimadzu, Changchun, China) at a displacement speed of 2 mm/min. Three specimens of each sample were tested and the average values were calculated as the tensile properties. In addition, the fracture behaviors of the samples were studied.

3. Results and Discussion

3.1. Microstructure

Figure 3 shows the microstructures of the forged and heat-treated TiC/2219 nanocomposites with different TiC nanoparticle contents (0, 0.5, 0.9, 1.3, and 1.7 wt.%). Compared with the 2219 alloy, the grains in all the nanocomposites became refined with the addition of TiC nanoparticles (Figure 3). As shown in Figure 3a, the grain size of the 2219 alloy was larger than that of the composites. As shown in Figure 3b–f, with an increase in particle content, the grain size of the composites decreased and then increased. The grain size of the 2219 alloy was 195 \( \mu \)m. At particle contents of 0.5 wt.% and 0.9 wt.%, the grain sizes were 163 \( \mu \)m and 78 \( \mu \)m, respectively. In addition, it was observed that a small amount of nanoparticles aggregated at the grain boundary of the 0.9 wt.% TiC/2219 nanocomposites as shown in Figure 3c in the enlarged part (1). Figure 4a,b shows that the TiC nanoparticles aggregated at the grain boundaries of the 0.9 wt.% TiC/2219 nanocomposite. The EDS analysis of the agglomeration is shown in Figure 4d. The TiC nanoparticles dispersed in the matrix (Figure 4c). However, with further increase in particle content to 1.3 wt.% and 1.7 wt.%, the grain size increased to 96 \( \mu \)m and 114 \( \mu \)m, respectively. Moreover, at a particle content of 1.7 wt.%, a large amount of sub-grains and agglomeration of nanoparticles appeared in the crystal and at the grain boundaries, respectively, as shown in Figure 3e and enlarged part (3). The EBSD orientation maps also showed sub-grains of TiC/2219 composites with different TiC nanoparticle contents, including 0 wt.%, 1.3 wt.%, and 1.7 wt.% as shown in Figure 5. The white lines in the images were small angle grain boundaries. The existence of sub-grains was thus proved.

Previous studies of as-cast samples found that the nanoparticles could uniformly disperse in the 0.9 wt.% TiC/2219 nanocomposite. As the particle content continued to increase, the particles enriched at the grain boundaries after reaching the threshold of particle incorporation into the matrix (Figure 3e). Figure 3c also shows the nanoparticles agglomerate at grain boundaries. This might be because each direction was only pierced once during the forging process, resulting in a low deformation rate, which could not induce an effective force to break the agglomerated particles. The same conclusion can be found in the literature [16]. The changes in the grain sizes of different samples were because an appropriate amount of nanoparticles could serve as heterogeneous nucleating centers during the
solidification process, thus decreasing the grain size. The more nanoparticles in the matrix, the more heat they absorbed, which led to a lower energy of deformation being stored in the material; thus, a strong dynamic recovery could be achieved [26]. Therefore, the number of nucleation sites formed during the solution treatment was small and most of the stored deformation energy could be used for grain growth; thus, the grain size gradually increased. With the continuous addition of particles, the storage energy, and the driving force of recrystallization further reduced, resulting in incomplete crystallization and sub-grains. In addition, dislocation loops were found around the precipitations as shown in Section 3.3. The extra dislocation caused by the nanoparticle could provide the driving force for recrystallization. Dislocation loops are shown in the following chapter. The evolution of the grain structure is not the subject of this study but will be discussed in another report.

Figure 3. Optical microscopy (OM) images of forged and heat-treated TiC/2219 nanocomposites with different nanoparticle contents: (a) 0 wt.%, (b) 0.5 wt.%, (c) 0.9 wt.%, (d) 1.3 wt.%, and (e) 1.7 wt.%. Inset (1) and (2) present the agglomerated TiC nanoparticles along the grain boundaries and sub-grains, respectively, and (3) represents the serious nanoparticle agglomeration along the grain boundaries; (f) is the average grain size of the TiC/2219 nanocomposites.

Figure 6 shows the SEM micrographs of the forged and heat-treated 2219 alloy and TiC/2219 nanocomposites with different TiC nanoparticle contents. The SEM images of the 2219 alloy shown in Figure 6a reveal a large number of coarse and continuous Al$_2$Cu phases along the grain boundaries, showing a network structure. Figure 6b,c show that with the increased TiC nanoparticle content, the coarse Al$_2$Cu phases in the matrix begin to decrease, forming discontinuous fine Al$_2$Cu phases. When the particle content increased to 1.3 wt.% and 1.7 wt.% (Figure 6d,e), the amount of Al$_2$Cu phases increased and many coarse network structures gradually formed. Figure 6f shows the area fraction of Al$_2$Cu phases in these samples. The area distributions of the Al$_2$Cu were measured by the software named Image pro plus. The SEM images of Al$_2$Cu were put into the software, then the software recognized different colors of the SEM image calculating the percentage of different color areas automatically. The amount of Al$_2$Cu phase in the 0.9 wt.% TiC/2219 nanocomposites was the smallest. With increasing TiC nanoparticle content from 0 wt.% to 0.9 wt.%, the area fraction of the Al$_2$Cu
phases decreased from 2.19% to 0.26% due to dissolution into the matrix. However, with increasing TiC nanoparticles content from 1.3 wt.% to 1.7 wt.%, the area fraction of the Al$_2$Cu phases increased from 0.83% to 1.16%. As shown in Figure 3, the grain size changed with the addition of nanoparticles. The smaller the grain size, the smaller the grain boundary. As a result, at a certain solution temperature, the Al$_2$Cu phases at the grain boundary of small grains could easily melt into the matrix than at the grain boundary of large grains. Hence, the phenomena shown in Figure 6b,c could occur. As the particle content increased, more nanoparticles concentrated at the grain boundaries, thereby inhibiting the dissolution of Al$_2$Cu phases, as shown in Figure 6d,e. The difference of the area fraction of Al$_2$Cu phases in different samples also directly indicated the influence of different TiC nanoparticle contents on the precipitation phase. The more precipitated phases there were, the more Al$_2$Cu phases precipitated into the crystals and the smaller the area fraction of Al$_2$Cu phases was. This is further explained in Section 3.2.

Figure 4. SEM micrographs of (a) aggregated TiC nanoparticles along the grain boundaries of 0.9 wt.% Table 2219. nanocomposite; (b) magnification SEM micrograph of the microstructure; (c) TiC nanoparticles dispersed in the matrix; (d) Energy Dispersive Spectrometer (EDS) results corresponding to the phase.
Figure 5. Electron backscatter diffraction (EBSD) orientation maps showing the sub-grain of TiC/2219 nanocomposites with different TiC nanoparticles contents: (a) 0% TiC, (b) 1.3% TiC, and (c) 1.7% TiC.

Figure 6. SEM images of the forged and heat-treated TiC/2219 nanocomposite with different nanoparticle contents: (a) 0 wt.%, (b) 0.5 wt.%, (c) 0.9 wt.%, (d) 1.3 wt.%, and (e) 1.7 wt.%; (f) the area fraction of Al2Cu phases in TiC/2219 nanocomposites.

3.2. DSC Analysis

Figure 7 shows the DSC curves of the forged and heat-treated TiC/2219 nanocomposites with different TiC nanoparticle contents. DSC was performed to determine the types of precipitated phases and show their relative contents in the matrix. In the DSC curve of the aluminum alloy, the endothermic peak represents the dissolution of phases and the exothermic peak represents the precipitation and growth of the precipitated phases. The DSC curves of the 2219 alloy and composite materials with different contents of 0.5, 0.9, 1.3, and 1.7 wt.% show endothermic peaks at 549.94, 550.8, 550.32, 550.74, and 550.82 °C, respectively (Figure 7a). The endothermic peaks of the composites shifted toward higher temperatures compared with that of the 2219 alloy due to an increase in thermal stability after addition of TiC nanoparticles. This is also probably caused by the variable alloying compositions, the externally added TiC particles, the potential as-cast impurity, and the specific experimental process. The addition of TiC slightly increases the solution temperature of the alloy. The precipitated phase at this point was the θ phase that was the Al2Cu phase. The areas of endothermic and exothermic peaks could reflect the enthalpy of phase transformation in alloys. The larger the volume fraction of the second phase, the larger the area of the corresponding peak. This is shown in Figure 7b, where the endothermic peak (V) of the composite is larger than that of the 2219 alloy, indicating a greater dissolution of Al2Cu phases in the composite. The exothermic peak (M) also increases with the addition of TiC, reflecting the growth of the precipitated phases. The difference of the area fraction of Al2Cu phases in different samples was directly indicated by the endothermic peak (W) for sample 1 (Figure 7b). The endothermic peak W for sample 1 was the biggest, which is consistent with the results in Figure 6. These results indicated that TiC nanoparticle content of 0.9 wt.% effectively promotes the mechanical strength of the 0.9 wt.% TiC/2219 composite. The micro-morphology of θ″ and θ′ phases is shown in Figure 8.

The smaller the grain size, the smaller the grain boundary. As a result, the smaller the volume fraction of the second phase in the alloys, the smaller the area of corresponding peak. These results indicated that TiC nanoparticle content of 0.9 wt.% effectively promotes the mechanical strength of the 0.9 wt.% TiC/2219 composite. The micro-morphology of θ″ and θ′ phases is shown in Figure 8.

Figure 7 shows the DSC curves of the forged and heat-treated TiC/2219 nanocomposites with different TiC nanoparticles contents: (a) 0% TiC, (b) 1.3% TiC, and (c) 1.7% TiC.
phase in the alloys, the larger the area of corresponding peaks. The area of endothermic W represented the amount of Al$_2$Cu phase. This proved that the Al$_2$Cu phase in the composite was lower than in the 2219 alloy. The endothermic peak W for sample A was noticeably bigger than other composites (Figure 7a), while the endothermic peak W of curve C was the smallest and the endothermic peak W of curve A was the biggest. This proved that a greater amount of Al$_2$Cu phase was present in sample A than in sample B, C, D, and E. This was consistent with the conclusion drawn from the results shown in Figure 6. And Figure 7b shows an endothermic peak V and an exothermic peak M in each curve. The endothermic peak V represented the dissolution of the θ” phase [27] and was largest for sample C. The exothermic peak M of sample C was the largest as well. These results indicated that TiC nanoparticle content of 0.9 wt.% effectively promoted the precipitation of θ” and θ’ phases. The amounts of θ” and θ’ phases played important roles in the mechanical strength of the 0.9 wt.% TiC/2219 composite. The micro-morphology of θ” and θ’ phases is shown in Figure 8.

![DSC heating curves of the forged and heat-treated TiC/2219 nanocomposite samples](image)

**Figure 7.** DSC heating curves of the forged and heat-treated TiC/2219 nanocomposite samples: (a) endothermic peak W represents the dissolution of phases, and (b) exothermic peak M represents the precipitation and growth of the precipitated phases.

### 3.3. TEM Observations

In an Al-Cu alloy, the typical aging precipitation sequence is as follows: Supersaturated solid solution → GP zone → θ” → θ’ → θ (Al$_2$Cu) [28]. The θ’ phases are formed on the (100)$_{α}$-Al planes in Al-Cu alloys [29]. Figure 8 shows the TEM bright-field micrographs of the plate-shaped θ’ phases in the forged 2219 alloy and composites with different nanoparticle contents subjected to the same T6 heat treatment. Figure 8a shows the presence of very few θ’ precipitates in the matrix. The average diameter and thickness of the θ’ phases in the 2219 alloy were about 124 nm and 6 nm, respectively, but the amount of θ’ phases was very small (Figure 8g). At a particle content of 0.9 wt.%, a large number of dense θ” and θ’ phases were present in the matrix (Figure 8c), and the distribution of θ’ phase was more homogeneous. The average diameter and thickness of the θ’ phases in it were about 171 nm and 7 nm, respectively (Figure 8i). With an increase in the TiC nanoparticle content, the number of θ’ phases began to decrease (Figure 8d,e). The average diameter and thickness of the θ’ phases in 1.3 wt.% TiC/2219 and 1.7 wt.% TiC/2219 composites were about 213 nm, 8 nm, and 287 nm, 8 nm, respectively (Figure 8j,k). Because the grain size of the composite was smaller than that of the alloy, the solution distance of the Cu atom became shorter during aging [30]. As described in Section 3.1, the area fraction of Al$_2$Cu was the largest. Therefore, compared with other composites, a large number of agglomerated Al$_2$Cu particles were not conducive to the precipitation in the precipitated phase under the same heat treatment process. In addition, dislocation loops were found around the precipitations (Figure 8e). Figure 8f shows the TEM morphology of TiC nanoparticles in the matrix. It can be seen that a particle content of 0.9 wt.% is beneficial for the precipitation of θ” and θ’ phases. This was also confirmed from Figure 7b. The addition of 0.9 wt.% TiC nanoparticles promoted the precipitation of the θ’ phase due to the presence of a larger amount of nanoparticles in the matrix. Hardy [31]...
considered that atoms considerably larger than Al could affect the nucleation of precipitated phases. The diameter of TiC nanoparticle (20–100 nm) was larger than that of the Al atom (0.143 nm). When TiC nanoparticles entered the Al matrix, it inevitably caused crystal lattice distortion and increased the system’s energy. To maintain low system energy, more oversaturated vacancies might aggregate around the TiC nanoparticles. With the addition of 1.3 wt.% and 1.7 wt.% TiC, the number of precipitated phases decreased, possibly because more particles were agglomerated at the grain boundaries, resulting in a decrease in the solid solubility of Cu atom in the aluminum matrix.

Figure 8. TEM micrographs of the forged and heat-treated TiC/2219 nanocomposite with different nanoparticle contents: (a) 0 wt.%, (b) 0.5 wt.%, (c) 0.9 wt.%, (d) 1.3 wt.% and (e) 1.7 wt.%. (g–k) the corresponding statistical results of the diameters of the θ’ precipitates in (a–f), respectively; (f) morphology of TiC nanoparticle in 0.9 wt.% TiC/2219 nanocomposite; (l) the TEM-EDS of the TiC nanoparticle.

3.4. Mechanical Properties

Figure 9 shows the effect of different TiC nanoparticle contents on the ultimate tensile strength (UTS), yield strength (YS), and elongation of all the samples. The numerical results are listed in Table 1. Compared with the 2219 alloy, the strength and elongation of the composites significantly improved.
The 0.9 wt.% TiC/2219 composite exhibited the highest strength and ductility. Combined with the results shown in Figure 7b, this implied that the sample was strengthened by the \( \theta'' \) and \( \theta' \) phases because the nano-precipitated phases were limited and hindered the drive and motion of the dislocations by forcing the dislocations around the nano-precipitated phase. This played an important role in increasing the material strength. Therefore, the size and volume fraction of \( \theta'' \) and \( \theta' \) phases affected the final properties of the materials. As can be seen from Figure 8c, composite with a nanoparticle content of 0.9 wt.% contains the highest number of precipitated \( \theta'' \) and \( \theta' \) phases, and thus exhibits a higher performance.

### Table 1. The tensile data of the 2219 alloy and the TiC/2219 composites with different particle contents at a displacement speed of 2 mm/min.

<table>
<thead>
<tr>
<th>TiC (wt.%)</th>
<th>( \sigma_{0.2} ) (MPa)</th>
<th>( \sigma_{UTS} ) (MPa)</th>
<th>( \delta_f ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>206</td>
<td>331</td>
<td>8.6</td>
</tr>
<tr>
<td>0.5</td>
<td>232</td>
<td>355</td>
<td>9.4</td>
</tr>
<tr>
<td>0.9</td>
<td>301</td>
<td>411</td>
<td>11.8</td>
</tr>
<tr>
<td>1.3</td>
<td>267</td>
<td>389</td>
<td>9.1</td>
</tr>
<tr>
<td>1.7</td>
<td>244</td>
<td>374</td>
<td>7.7</td>
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### 3.5. Strengthening of TiC/2219 Nanocomposite

The two major strengthening components in metal matrix composites (MMCs) included grain refinement and Orowan strengthening. After introducing the TiC nanoparticles, the grain refinement occurred with decreasing grain sizes. The smaller the grain sizes became, the more grain boundaries accommodated the plastic deformation. Usually, smaller grain size leads to higher yield strength (termed as Hall-Petch effect). Strengthening (\( \Delta \sigma_{GR} \)) from grain refinement in the MMCs is described in Equation (1) [32,33].

\[
\Delta \sigma_{GR} = k_{H-P} \left( \left( d_{mmc} \right)^{-1/2} - \left( d_{mm} \right)^{-1/2} \right)
\]

where \( k_{H-P}, d_{mmc}, \) and \( d_{mm} \) are defined as the Hall-Petch coefficient, the grain sizes of reinforced MMCs, and the grains sizes of unreinforced pure alloy matrix, respectively. \( k_{H-P} \) is 74 MPa \( \mu m^{1/2} \) [34].

The dislocation-particle interaction induces a dislocation loop surrounding the particle, further stimulating an increase in the mechanical strength. This kind of particle-induced strengthening mechanism is termed as Orowan strengthening. Such increasing strength is proportional to the inverse of inter-particle spacing. Orowan strengthening (\( \Delta \sigma_{OR} \)) is quantitatively evaluated by Equation (2).

\[
\Delta \sigma_{OR} = \frac{0.13 b G m}{d_p \left( 8 V_p^3 - 1 \right)} \ln \frac{d_p}{2b}
\]
In Equation (2), $b$ represents the Burger’s vector, $G_m$ is the shear modulus, $d_p$ designates the average nanoparticle size, and $V_p$ defines the volume fraction of nanoparticles. Regarding AA2219 Al alloy, the $G_m$ value is determined to be 25.4 GPa at 300 K [35]. Burger’s vector, $|b|$, is ~0.286 nm for Al alloys [36]. $V_p$ designates the volume fraction of reinforcing nanoparticles. $V_p$ can be obtained by solving Equation (3) [37].

$$\lambda = d_p \left[ \left( \frac{1}{2V_p} \right)^{\frac{1}{3}} - 1 \right]$$

(3)

$\lambda$ in Equation (3) defines the inter-particle spacing. In the present TiC/2219 nanocomposite, $\lambda$ should be evaluated from the TiC nanoparticles sitting inside the $\alpha$-Al matrix grains rather than those agglomerating at the $\alpha$-Al/$\alpha$-Al$_2$Cu eutectic networks or grain boundaries.

By substituting all the critical parameters into Equations (1)–(3), the individual contribution of two strengthening mechanisms to the yield strength ($\sigma$) of TiC/2219 nanocomposite with 0.9 wt.% TiC can be calculated. Orowan strengthening made the most significant contribution to the yield stress, with $\Delta \sigma_{\text{Orowan}}$ value of 68.15 MPa. The value of $\Delta \sigma_{\text{GR}}$ is 2.93 MPa.

3.6. Fracture Behavior

Figure 10 shows the fracture surfaces of the forged and heat-treated 2219 alloy and composites. Figure 10a shows that the fracture surface of the 2219 alloy has many coarse Al$_2$Cu phases and shallow dimples along with very few tear ridges. The main fracture mode was a transgranular fracture. Figure 10b shows many tear ridges and some big deep dimples, and the main fracture mode was ductile. Figure 10c shows many small deep dimples and tearing edges, which impart high ductility. The magnified image shows that TiC nanoparticles were distributed evenly in the dimples. Hence, the 0.9 wt.% TiC/2219 composite shows the best performance (Table 1). However, as the particle content increased, the number of dimples began to decrease and was accompanied by the coarse Al$_2$Cu phases (Figure 10d). The fracture mode was characterized by a combination of toughness and brittleness. At a nanoparticle content of 1.7 wt.%, the dimples became coarse and the amount of dimples decreased. In addition, the agglomerated nanoparticles were found at the grain boundaries (Figure 10e). In general, the ductile fracture was dominant. The uniformly dispersed nanoparticles in the matrix served as nucleation centers, resulting in the reduction of grain size. Therefore, more dimples were present on the fracture surface. With increasing nanoparticle content, more and more nanoparticles will accumulate at the grain boundaries forming clusters, which will cause some shrinkages and porosities, resulting in serious degradation of the material’s mechanical properties. In addition, the agglomerated TiC nanoparticles lead to the formation of voids/porosities between neighboring particles, resulting in an uncompact microstructure. The areas with such loose microstructures will, in turn, deliver mechanical anisotropy. Consequently, the corresponding mechanical properties deteriorated.
were drawn based on the obtained results:

(4) The mechanical properties of the forged and heat-treated 0.9 wt.% TiC

(2) An appropriate amount of TiC nanoparticles could promote the dissolution of Al

(1) After solution aging, usually very few sub-grains would exist in the matrix for the 2219 alloy. However, there were still many sub-grains in composites with 1.3 wt.% TiC and 1.7 wt.% TiC as shown in the EBSD.

(2) An appropriate amount of TiC nanoparticles could promote the dissolution of Al\textsubscript{2}Cu particles during heat treatment. With increasing TiC nanoparticle content from 0 wt.% to 0.9 wt.%, the area fraction of the Al\textsubscript{2}Cu phases decreased from 2.19% to 0.26% due to dissolution into the matrix. However, with increasing TiC nanoparticle content from 1.3 wt.% to 1.7 wt.%, the area fraction of the Al\textsubscript{2}Cu phases increased from 0.83% to 1.16%.

(3) For the forged and heat-treated composites, the addition of TiC nanoparticles facilitated the precipitation of \(^\theta''\) and \(^\theta'\) phases during aging. At a nanoparticle content of 0.9 wt.%, the largest amounts of \(^\theta''\) and \(^\theta'\) phases precipitated in the matrix. However, with a further increase in TiC nanoparticles content, the precipitation of the precipitated phase was inhibited. When TiC nanoparticles entered the Al matrix, it inevitably caused crystal lattice distortion and increased the system’s energy. To maintain low system energy, more oversaturated vacancies might aggregate around the TiC nanoparticles. This was the reason for the many precipitates in the 0.9 wt.% TiC/2219 nanocomposite.

(4) The mechanical properties of the forged and heat-treated 0.9 wt.% TiC/2219 nanocomposite were better than those of the 2219 alloy and other composites. The tensile strength, yield strength, and elongation of the forged 0.9 wt.% TiC/2219 nanocomposite increased by 24.2%, 46.1%, and 37.2%, respectively, than those of the forged 2219 alloy.

Figure 10. Fracture surfaces of the forged and heat-treated TiC/2219 nanocomposite with different nanoparticle contents: (a) 0 wt.%, (b) 0.5 wt.%, (c) 0.9 wt.%, (d) 1.3 wt.%, and (e) 1.7 wt.%, respectively.

4. Conclusions

In this work, the effects of different nanoparticle content (mass fractions) on the precipitation phase of the forged and heat-treated TiC/2219 nanocomposites were studied. The following conclusions were drawn based on the obtained results:

(1) After solution aging, usually very few sub-grains would exist in the matrix for the 2219 alloy. However, there were still many sub-grains in composites with 1.3 wt.% TiC and 1.7 wt.% TiC as shown in the EBSD.

(2) An appropriate amount of TiC nanoparticles could promote the dissolution of Al\textsubscript{2}Cu particles during heat treatment. With increasing TiC nanoparticle content from 0 wt.% to 0.9 wt.%, the area fraction of the Al\textsubscript{2}Cu phases decreased from 2.19% to 0.26% due to dissolution into the matrix. However, with increasing TiC nanoparticle content from 1.3 wt.% to 1.7 wt.%, the area fraction of the Al\textsubscript{2}Cu phases increased from 0.83% to 1.16%.

(3) For the forged and heat-treated composites, the addition of TiC nanoparticles facilitated the precipitation of \(^\theta''\) and \(^\theta'\) phases during aging. At a nanoparticle content of 0.9 wt.%, the largest amounts of \(^\theta''\) and \(^\theta'\) phases precipitated in the matrix. However, with a further increase in TiC nanoparticles content, the precipitation of the precipitated phase was inhibited. When TiC nanoparticles entered the Al matrix, it inevitably caused crystal lattice distortion and increased the system’s energy. To maintain low system energy, more oversaturated vacancies might aggregate around the TiC nanoparticles. This was the reason for the many precipitates in the 0.9 wt.% TiC/2219 nanocomposite.

(4) The mechanical properties of the forged and heat-treated 0.9 wt.% TiC/2219 nanocomposite were better than those of the 2219 alloy and other composites. The tensile strength, yield strength, and elongation of the forged 0.9 wt.% TiC/2219 nanocomposite increased by 24.2%, 46.1%, and 37.2%, respectively, than those of the forged 2219 alloy.
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