Effect of La on microstructures and mechanical properties of Cu/Ti₃SiC₂/C nanocomposites sintered by vacuum hot-pressing and hot isostatic pressing

Lan Lv¹,², Xiao-Song Jiang¹,², Mei-Mei Zhang¹,², Hong-Liang Sun¹,², Zhen-Yi Shao¹,², Ning-Ning Fu¹ and Wen-Tao Jin²

¹ Key Laboratory of Advanced Technologies of Materials, Ministry of Education, Chengdu 610031, People’s Republic of China
² School of Materials Science and Engineering, Southwest Jiaotong University, Chengdu Sichuan 610031, People’s Republic of China
³ CRRC Puzhen Co., Ltd, Nanjing, Jiangsu 210031, People’s Republic of China

E-mail: xsjiang@swjtu.edu.cn

Keywords: La, hot pressing, hot isostatic pressing, copper matrix composites, mechanical properties

Abstract

Researches have shown that the addition of trace amounts of rare earth element lanthanum (La) to the alloys and composites can significantly improve their microstructure and properties. In this work, Cu/Ti₃SiC₂/C composites with 0.05wt%, 0.1wt% and 0.3wt% La were prepared by powder metallurgy method through mechanical alloying, hot-pressing (HP) and hot isostatic pressing (HIP). The effects of different La contents on the microstructure and mechanical properties of Cu/Ti₃SiC₂/C composites were investigated. The results show that La has a refinement effect on the grain of the matrix, and with the increase of La content, the size of the matrix of the composite becomes smaller. As the content of La increases, the performance of the composite exhibits a tendency to increase first and then decrease. The composite of 0.1wt% La exhibited the best performance with a hardness of 97.8 MPa, a tensile strength of 174.9 MPa, and a compressive strength and shear strength of 461.1 MPa and 102.1 MPa, respectively. Since the dimple is observed, the tensile fracture indicates that the fracture mode is a ductile fracture. The enhancement mechanism of La mainly includes dispersion strengthening and fine grain strengthening.

1. Introduction

Cu/Ti₃SiC₂/C nanocomposites have good electrical conductivity, thermal conductivity and electrical conductivity, thus are widely used in the manufacture of automotive radiators, ship heat exchanger condensation plates, brake pads and corrosion resistant parts [1–3]. Ti₃SiC₂ possesses high hardness, high melting point as well as excellent oxidation resistance and strength under the high temperature, which increases the bearing particles on the substrate and acts as a dispersion strengthening effect in the composite material to further improve the mechanical properties of composite materials [1]. Graphene nanoplatelets (CNP₃) and Carbon nanotubes (CNT₃) have similar atomic structures and are widely used in composite materials because of their high modulus of elasticity and high wear resistance. Graphite-reinforced Cu/Ti₃SiC₂/C nanocomposites have been practically applied as slider materials because of its good electrical conductivity and excellent resistance to arc erosion [4]. However, owing to the grain growth of the composite and the occurrence of agglomeration during the sintering process as well as the poor wettability with Ti₃SiC₂, CNP₃, CNT₃, etc, the load transfer efficiency of the carbon material in the Cu matrix and the strengthening effect can be reduced [5–7].

In order to improve the performance of the Cu matrix composite, it is necessary to avoid coarse grains and agglomeration of enhanced phases. Tang et al [8] have shown that La has a certain positive impact on the microstructure and properties of metal composites. Adding rare earth elements in Cu can improve the microstructure and mechanical properties of Cu. Moreover, the rare earth elements have high chemical activity,
unique physical properties and stable chemical properties, which can significantly refine the grain structure of the alloy matrix, remove impurities as well as significantly improve the tensile strength of the material [9, 10]. Xue et al [11] showed that rare earth metal was a surface active element, which could reduce the surface tension of the metal matrix and improved the fluidity of the metal matrix. The weakness of surface tension resulted in a corresponding increase in the wettability of the reinforcing phase particles in the metal matrix, thus surface diffusion coefficient of the reinforcing phase particles was increased. In addition, the rare earth metal has low solid solubility in the metal matrix and was easily adsorbed at the phase boundary, which not only can be filled the interface defects, but also increased the interfacial energy between the reinforcing phase particles and the metal matrix. Hence, relatively dispersed reinforcing phase particles are prone to be formed in the metal matrix [10, 12]. Among rare earth elements, La is a light rare earth element with low hardness, high melting point, high boiling point and high densities. Chen et al [9] pointed out that La could refine the grain of Cu and also improved the grain structure of Cu. In addition, the addition of trace amounts of La will result in the formation of columnar grains. And the addition of appropriate La can inhibit the transform from columnar grain structure to equiaxed grain structure. During the process of preparation, a second phase of Cu₆La was formed, which was beneficial for the refinement of grains. During the stretching process, the ultimate tensile strength increases slowly due to the solid solution strengthening effect of the La atom. When the combination of fine grain strengthening and second phase particle strengthening, the ultimate tensile strength shows a sharp increase [13, 14]. And La is easy to react with O, S or P to form high melting point compounds. Furthermore, it can reduce the content of impurity and prevent the formation of harmful inclusions to improve the purity of the alloy. Compared with S, P, etc, the rare earth elements are easier to segregate at the grain boundary. The position of the grain boundary is preferentially occupied by them, and the S and P which are segregated at the grain boundary are reduced. Therefore, the weakening effect on the grain boundary is eliminated, and the grain boundary is purified [15, 16]. Inoue et al [17] found that the solid solubility of La atoms in the Al–La–Cu alloy is very low, thus its concentration in the front of liquid phase was increased, resulting in a component supercooling zone. During solidification, it can reduce the surface tension of the nucleus, promote nucleation of grains, increase the diffusion activation energy of the atoms and hinder growth of grain. In addition, La also forms high melting point compounds with certain elements in the matrix, which can act as a nucleation core to promote refinement of grains during solidification [18].

The starting point of this experimental design is to study the effect of La on the multi-phase reinforcement Cu-based composites. In this paper, the micro-nano composite structure of nano-reinforced phase and micro-matrix is constructed, and the formation and strengthening mechanism of multi-phase interface is established. It is hoped that the nano-enhanced phase and the Cu matrix can coexist in multiple phases, the uniform distribution of the nano-enhanced phase, and the enhancement of the phase enhancement of the nano-phase and the La interface, achieving the purpose of application in various fields. Among them, the specific surface area of the CNP₅ is large, which is advantageous for increasing the contact area with the substrate and promoting the interface with the substrate [5]. The CNP₅ is thinner and the gap between the matrix grains is very small, which facilitates the transfer of external forces from the Cu matrix to the CNP₅ [6, 7]. The ultra-high strength of CNP₅ can be directly used to achieve material reinforcement. Based on the ultra-high aspect ratio of CNTP₅, it can achieve fiber-like reinforcement in polymers. The bonding force between the Ti₃SiC₂ layers is weak [1]. If an external force is applied to the structure, the layer will easily slide between the layers and will provide good lubrication during friction and wear. Therefore, La–Cu/Ti₃SiC₂/C nanocomposites were prepared by mechanical alloying, hot pressing and hot isostatic pressing of rare earth elements La, CNP₅ nanosheets, CNT₅, graphite and Ti₃SiC₂. The effects of different La contents on the microstructure and mechanical properties of Cu/Ti₃SiC₂/C nanocomposites were investigated. In addition, the reinforcement and fracture mechanism of composite materials were studied in detail.

2. Experiment

2.1. Experimental materials
In this experiment, Cu powder (250 mesh), La powder (300 mesh), CNT₅ (20–30 nm in diameter, length: 10–30 μm), CNP₅ (number of layers < 10), Ti₃SiC₂ (300 mesh) and graphite (200 mesh) were used as raw materials. The specific composition is shown in table 1.

2.2. The composites fabrication
According to the design components of table 1, the raw materials was put into the polyurethane ball mill tank in turn, then added the appropriate amount of tert butyl alcohol (TBA) as the mixing medium. First, the La–Cu/C raw powder materials were ball-milled for 20 min. Second, powder materials were ball-milled for 1h with the addition of Ti₃SiC₂ and graphite. Then, the uniformly mixed material was taken out from the ball mill jar and...
then subjected to sufficient freeze-drying treatment on a freeze dryer (FD-A-50). The specific conditions of the freeze-drying treatment are: a temperature of −50 °C, a vacuum of 24 Pa, and a freeze-drying time of 24–48 h. Finally, the freeze-dried powder was processed by vacuum hot pressing (950 °C × 2 h × 20 MPa) and hot isostatic pressing (900 °C × 2 h × 100 MPa), and the process flow is shown in figure 1. The specific process curve of vacuum hot press sintering and hot isostatic pressing is shown in figure 2.
3. Results and discussion

3.1. Microscopic morphology analysis of the composites powder

Figure 3 is the SEM image of a Cu-based composite powder with different La contents, and table 2 shows the EDS results. As can be seen from figures 3(a)–(c), CNPS and graphite are dispersed in the composite. Figure 3(d) shows that CNPS is distributed on the boundary of Cu particles, the surface is smooth, and there is no wrinkle, indicating that the dispersion effect of CNPS is ideal, and the ball mill has not caused damage to its structure. It was found that the dot scan result of the point 1 in figure 3(e) can be judged as graphite. The EDS result of point 2 in figure 3(e) can be judged as a Cu matrix. The effect of ball-milling mixture on the impact, rolling and shearing of the powder is also related to the hardness of the powder itself. The hardness of the electrolytic copper in the powder is the lowest, and the deformation is most likely to occur during the high-speed mixing process. It is close to an elliptical shape and the copper particles are bonded to each other, which can be clearly observed in figure 3(e). In figure 3(f), the point 3 is judged as La. It can be seen that a large amount of La aggregates in the matrix because the atomic radius of the La is larger than the atomic radius of Cu. If it enters the Cu lattice, it will cause large lattice distortion to increase the system energy. Hence, it is difficult to form a solid solution between the La and the Cu element. In order to keep the system free energy possessing a minimum, La can only be enriched on the irregular grain boundaries. Moreover, the compounds accumulated on the grain boundaries can prevent growth of grains and increase the strength of the Cu alloy [13]. Li et al. [19] found that if a small amount of La is added to Cu, La element will be concentrated in front of the solid-liquid interface during solidification because of its low solid solubility. Therefore, the under cooling of Cu fluid can be increased during solidification process, and the grains of pure Cu grow in a columnar shape. The addition of La can also purify the Cu liquid and reduce the interference of impurities, thus contributing to the formation of columnar crystals [13]. From the results of table 2, the rare earth element of La (point 3) has a higher oxygen content, which indicates that the La is oxidized. Because La possessing an active chemical characteristic can be reacted with O, S, P, etc. to form high melting point compounds, which can reduce the amount of impurities and prevent the formation of harmful inclusions to purify the alloy [15, 16]. Chen et al. [9] studied the effects of La on properties of Cu and found that La easily reacts with impurity elements such as O and S in Cu to form La2O3 and La2O2S compounds, which can also refine grains. Because La2O3 and La2O2S have higher melting points than Cu, they are first solidified. These previously solidified phases provide sufficient nucleation centers to accelerate the nucleation process of the Cu grains and prevent pinning and drag grain boundary effects, thereby refining the Cu grains [20].

3.2. Microscopic morphology analysis of the composites

Figures 4(a)–(c) shows the optical micro-morphology of the microstructure of Cu-based composites with different La contents. Figures 4(d) and (e) show the optical images of 0.1wt% La composite in the radial and axial directions. Figure 4(f) is a schematic view of the sintered samples. From these morphologies, there are many black areas, the long black areas are added graphite, CNTs or CNPS. The black areas that are irregularly distributed and do not repeat in different samples are Holes. The continuous distribution of white areas is the Cu, and the gray phase is titanium silicon carbon or other phases. It can be seen from figures 4(a)–(c) that the reinforcing phases are not agglomerated, indicating that La can reduce the surface tension of Cu, so that the wettability and surface diffusion coefficient of the reinforcing phase particles in the Cu matrix increase to form a relatively dispersed morphology [11]. Zou et al. [21] also mentioned that the distribution of reinforcing phase particles in Cu was also improved after the addition of La. From the severe aggregation to the relative dispersion, the addition of La reduces the surface tension of the solid-liquid interface, resulting in a decrease in the contact angle, thereby obtaining a better liquid-liquid interface wettability.

Figure 4(f) is a schematic view of the sintered body, which is axial in the direction parallel to the pressing pressure and radial in the direction perpendicular to the pressing pressure. The specimen was prepared by...
powder metallurgy and the resulting bulk material was anisotropic. It can be seen from figures (d) and (e) that the axial and radial microstructure of the composites material are different. The black metallographic structure is elongated and the thickness is not equal, which is obviously due to the pressure during hot pressing. The dark gray and light gray metallographic structures have no obvious directionality because the same pressure is applied in all directions during the hot isostatic pressing to cause the directionality of the green body to be improved.

Figure 3 is an XRD diffraction pattern before and after sintering of different La content composite powders. It can be seen from the figure (a) that there is a spectral line of La, and the added reinforcing phase can find the

Table 2. Atomic percentage of each element of points in figure 3 (at%).

| Point | C(at%) | Cu(at%) | La(at%) | Ti(at%) | Si(at%) | O(at%) |
|-------|--------|---------|---------|---------|---------|--------|
| 1     | 95.55  | 4.45    | —       | —       | —       | —      |
| 2     | 0.92   | 99.08   | —       | —       | —       | —      |
| 3     | 3.30   | 15.37   | 16.67   | —       | —       | 64.65  |
Figure 4. (a)–(c) Optical micrograph of composites with different La content; (d), (e) Optical micrographs of radial and axial directions of 0.1 wt% La composite; (f) Sintered body schematic.

Figure 5. (a) XRD diffraction pattern of composite powder with different La content before sintering; (b) XRD diffraction pattern of composite powder with different La content after sintering.
corresponding diffraction peak, indicating that each raw material exists in its own form in the mixed powder without any reaction or change. It can be seen from (b) that the diffraction peak of C disappears, the diffraction peak of TiC appears in (200) and (220), and the diffraction peak of Ti$_3$SiC$_2$ becomes weak, indicating that the decomposition reaction of Ti$_3$SiC$_2$ occurs during sintering. The TiC phase is formed, and it is presumed that a reaction as shown in (1) may occur during sintering. According to Gibbs free energy calculation, as in formula (2), the Gibbs free energy $\Delta rG_m = -231.68 \text{ kJ mol}^{-1}$ obtained at 1200 K, the reaction proceeds in the forward direction. Ngai et al [22] synthesized Cu/Ti$_3$SiC$_2$ metal matrix composites, and pointed out that at 800 $^\circ$C, Ti$_3$SiC$_2$ will decompose to form a large amount of SiC, TiC and TiSi$_2$, but excessive TiC and other substances will reduce the lubricating properties of the composite. The temperature can be chosen to be reduced during preparation.

$$\text{Ti}_3\text{SiC}_2 = 3\text{TiC}_2/3 + \text{Si}$$  \hspace{1cm} (1)

$$\Delta rG_m = \sum \gamma_B \Delta rG_m$$  \hspace{1cm} (2)

Table 3 shows the matrix grain size of composite materials with different La content. The variation of line width and grain size can be reflected by Scherrer formula [23] such as (3):

$$\beta = \frac{K \lambda}{L \cos \theta}$$  \hspace{1cm} (3)

$\beta$ is the half width and height (radian) of the diffraction peak; $L$ is the size of the crystal lattice in the normal direction of the reflective crystal plane; when the linearity of the spectral line is Gaussian, and the crystal lattice is a uniform cube, $K$ is a constant, approximately equal to 1. From this, the size of a crystal face in the crystal or the average size of the crystal is estimated.

Table 3 is the grain size after sintering of the composite materials with different La contents estimated according to the Scherrer formula. According to Hall-Petch relation [24], as shown in equation (4), the intensity is inversely proportional to the grain size. It shows that refining the grains can increase the strength. It can be seen from table 3 that as the La content increases, the size of the matrix grains of the composite material becomes smaller, indicating that La has a refinement effect on the grain of the matrix. It is seen in figure 3(f) that La accumulates at the grain boundaries, and the compound accumulated on the grain boundaries can prevent grain growth. Zhou et al [13] prepared Cu doped without La and Cu doped with La, and the former was found to have a larger grain size. La collects on the grain boundaries and prevents grain growth. At the same time, La reacts with impurities such as lead and antimony in Cu to form a high melting point compound, which can purify. These compounds have a bulbous shape and are evenly distributed in the matrix, which inhibits the growth of the matrix. Thereby refining the grains and increasing the high temperature strength [16]. However, at 800 $^\circ$C and above, the Ti$_3$SiC$_2$ particles are unstable, and the decomposition of Ti$_3$SiC$_2$ will lead to the formation of carbides such as TiC and TiSi$_2$. The presence of these brittle phases hinders the diffusion of Cu and grain growth, which inhibits its densification process [22]. Mechanical alloying time has a certain effect on particle size. Ružić et al [24] pointed out that the particle size of the powder increases at the beginning of the ball milling, and the particle size reached a peak at 5 h after ball milling. The particle size then begins to decrease and reaches a minimum at 20 h. After further ball milling, the particle size of the powder increases again. In this experiment, the ball milling time was 80 min which did not play a large role in reducing the particle size.

$$\sigma_s = \sigma_0 + Kd^{-1/2}$$  \hspace{1cm} (4)

$\sigma_s$ — yield strength, $\sigma_0$ — the peierls stress, $K$ — the lattice disorder strength coefficient, $d$ — grain diameter.

### 3.3. Densities of the composites

Table 4 shows the relative densities results of Cu-based composites with different La contents. It can be seen from the results in the table that the densities of the samples after sintering is as high as 99%. With the increase of La content, the densities first rises and then decreases slightly. Due to the addition of La, the surface tension of the Cu matrix is reduced to increase the wettability, so that the particles in the composite are easy to move, can be

| La content | Average grain size (nm) |
|------------|-------------------------|
| 0.05 wt%   | 36.928                  |
| 0.1 wt%    | 33.936                  |
| 0.3 wt%    | 32.839                  |

### Table 3. The size of crystalline grain under different La content.
uniformly dispersed in the Cu matrix, and the pores are filled, thereby increasing the densities [25]. Gu et al [10] studied the WC-Co particle reinforced Cu matrix composites and found that the WC particles in the La2O3-free material have a severe agglomeration with a theoretical densities of only 79.8%. After the addition of La2O3, the significantly refined WC reinforcing particles were uniformly dispersed in the matrix, showing little aggregation, and a theoretical densities of 91.3% was obtained. As a typical surface active element, La atom has a surface tension much lower than that of molten Cu, which significantly reduces the surface tension of the molten material, which has a great influence on the dispersion state of the reinforcing particles and can improve the densification [26]. However, when La is excessive, La will be agglomerated in the Cu matrix. The volume of La atoms is larger than that of Cu atoms, and the agglomerated La is easy to form voids, so that the densities cannot continue to rise.

### 3.4. Mechanical properties of the composites

Figure 6(a) shows the hardness curves of the composites with different La contents. It can be seen that the hardness value of the composite increases with the increase of La content, indicating that the addition of La can increase the hardness of the Cu matrix composite. In combination with the particle size of Table 3, the effect of La grain refinement can improve the hardness of the material. Zhang et al [27] studied the mechanical properties of Cu composites, and the hardness of the composites showed a significant improvement, from 135 HV to 140 HV, mainly due to the addition of La to refine and disperse other particles. Fu et al [28] studied the effect of La2O3 on the microstructure and properties of Cu alloys, and found that when the content of La2O3 increased to 0.2%, the hardness reached a maximum. When the La content is too large, the alloy structure exhibits thick black and gray flakes, the distribution is uneven, and the surface also contains a large number of pores, and the relative densities and hardness of the alloy are lowered.

Figure 6(b) shows the shear strength of Cu-based composites with different La contents. The results in figure 6(b) show that the shear strength of the composites is not significantly improved. In general, composite interfacial bonding can be divided into four types: mechanical bonding, physical bonding (Van Der Waals interaction), diffusion bonding, and reaction bonding, and the binding force is sequentially increased [28]. Most of the reinforcing phases such as Cu and CNPS are mechanically bonded together, and the bonding strength is low. And in the shear test, the shear force is parallel to the radial direction of the sample. In the fracture scan of figure 7, it can be seen that the CNPS structure in the radial direction is elongated or flake-shaped, and the strip-like or sheet-like shearing ability is weak. Because CNPS and Cu have poor wettability, they are mainly mechanically bonded and physically combined. Although CNPS has high strength in the planar direction, it has low strength in the thickness direction, but this unidirectional load transfer mechanism affects the strengthening efficiency. Sinha et al [29] studied the effect of interface carbide layer on Cu alloy and found that the strengthening effect of CNPS is not only related to the performance of CNPS itself, but also the interface between CNPS and matrix and the spatial distribution of CNPS in the matrix.

Figure 6(c) shows the average tensile strength of composites with different La contents, and figure 6(d) shows the tensile stress-strain curves for composites with different La contents. It can be seen from figure 6(c) that the tensile strength of the composite increases with the increase of La content, and the tensile strength of the composite reaches a maximum of 174.91 Mpa when the La content is 0.1 wt%. It can be seen from figure 6(d) that in the initial stage of stretching, the curve is roughly in a straight line, and the material is mainly plasticized. La diffuses in the Cu matrix, acts as a dislocation source to increase the dislocation densities, and is distributed at the particle interface, which hinders dislocations and grain boundary motion, thereby increasing its strength. La is concentrated on the Cu grain boundary, as shown in figure 3(f), the compound accumulated on the grain boundary can prevent grain growth, inhibit static and dynamic recrystallization, and have the effect of refining crystal grains [30]. However, when the content of La is excessive, the strengthening effect on the deformation resistance of the matrix is not obvious. The La particles are concentrated on the grain boundaries of the Cu grains. This uneven structure causes defects in the interface of Cu particles and generates a brittle phase of Cu6La. The defect acts as a crack source to accelerate the fracture of the material under stress, and the tensile strength shows a downward trend [9]. Therefore, when the La content increases from 0.05 wt% to 0.1 wt%, the tensile strength increase of the Cu matrix composite is mainly due to the dispersion strengthening and fine grain strengthening of the La element. When La increases from 0.1 wt% to 0.3 wt%, the tensile strength of the material

| Table 4. The relative densities of Cu matrix composite in different La contents. |
|---------------------|-----------------|-----------------|-----------------|
| La(wt%) | Actual densities (g cm⁻³) | Theoretical densities (g cm⁻³) | Densities(%) |
| 0.05   | 7.26                        | 7.29                         | 98.89        |
| 0.10   | 7.21                        | 7.29                         | 99.54        |
| 0.30   | 7.22                        | 7.28                         | 99.01        |
decreases mainly because a large amount of La element is enriched in the Cu grain boundary and forms a Cu$_6$La brittle phase with Cu [9]. Brittle fracture grains were also found in the fracture scan of figure 7. Zou et al [21] studied the effect of La on the properties of Cu-based composites, and concluded that the maximum stress elongation increases with the addition of La, which is due to the refinement of grains and the solid-liquid interface. The surface tension is lowered, resulting in a decrease in the contact angle, resulting in better wettability [10]. Thus, sufficient wetting between the liquid and the reinforcing phase particles results in a significant smoothing of the initially irregularly shaped particles, resulting in more rounded reinforcing particles. However, the more La is added, the more agglomeration will occur in the Cu matrix, which will make the size and morphology of the reinforcing phase particles worse, thus affecting the mechanical properties.

Figure 6 (e) shows the compressive strength of Cu-based composites with different La contents, and (f) the compressive stress-strain curves of Cu-based composites with different La contents. Cu has good plasticity and generally undergoes severe deformation during compression without breaking. However, from the compression results, the material does not show good plasticity. The main reason for the compression fracture is that in the Cu matrix composite, a lot of reinforcing phase is added, and the reinforcing particles are not dissolved in the Cu matrix and are accumulated in the Cu matrix. The agglomerated La can be seen from figure 3(f). The enhanced
phase of these agglomerations hinders the movement of the grain boundaries and reduces the plasticity of the copper, thereby reducing the compressive capacity [9].

3.5. Fracture analysis of the composites

Figure 7 is a scanning fracture morphology of the composite material, and table 5 is the result of the EDS point scanning. Figures 7(a), (c), (e) are tensile fracture map of the composite material of 0.05 wt%, 0.1 wt%, 0.3 wt% La content. It can be seen that there are equiaxed dimples in the fracture, indicating that the material is plastically fractured. At the same time, there are many holes that are formed because the reinforcing phase is pulled out when the material breaks, as shown in figure 8. This is a schematic diagram of the CNTs being pulled out, leaving holes in the original position after tensile fracture [31]. Moreover, the CNTs can act like fiber strengthening on the matrix, and such a fracture mode increases the tensile strength. Yang et al [5] studied the load transfer of Cu/Ti3SiC2/C nanocomposites and pointed out that in the tensile failure process, the reinforcement phase forms a bridge spanning the upper and lower crack faces in the initial stage of the crack. As the load displacement increases, the relatively small end of the embedded length will be separated and pulled out of the matrix, indicating that the load is transferred to the reinforcing phase, thereby increasing the tensile strength [32]. It can be seen from figure 7(a) that the layered structure of CNPS is embedded in the Cu matrix, indicating that it is
better to bond with the Cu matrix. CNP$_S$ has a large surface area, which increases the contact area with the substrate and promotes interface bonding. A well-bonded interface can hinder dislocation movement because during the crack propagation process, the distance that the dislocation needs to be bypassed is increased [33, 34]. Moreover, during the stressing process of the composite material, the pleated structure of the CNP$_S$ is first flattened and then fractured, thereby exerting a buffering force effect. Chu et al [28] studied the strength of CNP$_S$-Cu composites, suggesting that the addition of CNP$_S$ below 8 vol% can significantly increase the yield strength and Young’s modulus to 114% and 37%, respectively. Because of the effective pinning effect of CNP$_S$ on the grain boundaries, dislocation motion can be prevented in the grain boundaries. As the La content increases, the equiaxed dimples become less, and brittle fracture grains appear in figure 7(e). It will show that more La is enriched in Cu, and La will combine with Cu to form a brittle phase of Cu$_6$La, which will affect the plasticity of the material. Chen et al [9] pointed out that the second phase of Cu$_6$La is formed during the preparation process, which can refine the grains, but excessive Cu$_6$La will cause brittle fracture.

In the figures 7(c) and(e), larger pieces of graphite particles can be seen, and graphite plays a large role in the wear reduction of the composite material. However, the graphite itself has a layered structure, and the layer stack size is large, and the wettability with Cu is not ideal. After the applied load, the pores are most easily formed at the graphite deposit, which eventually leads to material failure. Therefore, while ensuring the good anti-wear effect of graphite in the later stage, reducing the porosity caused by graphite is the focus of research on the performance of Cu-based composites.

### Table 5. Atomic percentage of each elements of points in figure 7(at%).

|   | C (at%) | Cu (at%) | La (at%) | Ti (at%) | Si (at%) |
|---|---------|----------|---------|---------|---------|
| 1 | 30.24   | 59.17    | 0.13    | 8.60    | 1.86    |
| 2 | 15.07   | 80.75    | 0.29    | 0.60    | 3.29    |
| 3 | 47.55   | 46.10    | —       | 4.39    | 1.95    |
| 4 | 4.41    | 84.87    | 0.01    | 8.05    | 2.66    |
| 5 | 2.75    | 57.11    | —       | 36.75   | 3.39    |

Figure 8. Schematic diagram of CNP$_S$/CNT$_S$ stretching.
4. Conclusion

In this paper, La-Cu/Ti$_3$SiC$_2$/C nanocomposites were prepared by mechanical alloying, hot-pressing and hot pressing isostatic pressing. The microstructure and mechanical properties of the composites were studied and analyzed, and the following conclusions were obtained:

1. The dispersed treated CNPs and CNTs have no severe agglomeration in the matrix, and there is also a good bond between the two. The graphite particles distributed in the composite powder are large, and the La content will agglomerate after reaching a certain value.

2. The observation of the crystal phase microstructure shows that the microstructure of the composite material has a directional strip shape in the radial direction perpendicular to the direction of the pressing pressure, and the crystal phase in the axial direction is uniform in structure. The densities of the sample is substantially as high as 99%, demonstrating that the green body prepared by the process is substantially densified. However, with the increase of La content, the densities of the composites first decreases and then rises, but the maximum amplitude does not exceed 1%. When the La content is 0.1 wt%, the densities of the composites reaches the lowest value. This is because the porosity of the Cu-based composite material is the largest when La and its oxide content is 0.1 wt%.

3. During the sintering process, Ti$_3$SiC$_2$ undergoes a decomposition reaction to form a new TiC phase. And as the La content increases, the size of the composite matrix becomes smaller, indicating that La has finer crystal grains in the microstructure of the matrix.

4. As the content of La increases, the performance of the composite exhibits a tendency to increase first and then decrease. 0.1 wt. The composite of %La exhibited the best performance with a hardness of 97.8 MPa, a tensile strength of 174.9 MPa, and a compressive strength and shear strength of 461.1 MPa and 102.1 MPa, respectively. Since the dimple is observed, the tensile fracture indicates that the fracture mode is a ductile fracture. The enhancement mechanism of La mainly includes dispersion strengthening and fine grain strengthening.

Acknowledgments

This work was funded by National Natural Science Foundation of China (No. 51201143), China Postdoctoral Science Foundation (No. 2015M570794, No. 2018T110993), R&D Projects Funding from the Research Council of Norway (No. 263875/H30).

ORCID iDs

Lan Lv @ https://orcid.org/0000-0002-3424-2986
Xiao-Song Jiang @ https://orcid.org/0000-0002-6703-9116

References

[1] Strojny–Nedza A, Pietrzak K and Węglewski W 2016 The influence of Al$_2$O$_3$ powder morphology on the properties of Cu–Al$_2$O$_3$ composites designed for functionally graded materials J. Mater. Eng. Perform. 25 3173–84
[2] Simoncini A, Tagliaferri V and Ucciardello N 2017 High thermal conductivity of copper matrix composite coatings with highly-aligned graphite nanoplatelets Materials (Basel) 10 1226
[3] Tubio C R, Antelo J, Guittian F and Gil A 2018 3D printed composites of copper–aluminum oxides 3D Print Addit Manuf. 5 46–52
[4] Kulkarni D D, Choi I, Singamaneni S S and Tsukruk V V 2010 Graphene oxide–polyelectrolyte nanomembranes ACS. Nano. 4 4667–76
[5] Yang M, Weng L, Zhu H, Zhang F, Fan T and Zhang D 2017 Leaf-like carbon nanotube-graphene nanoribbon hybrid reinforcements for enhanced load transfer in copper matrix composites Scripta. Mater. 138 17–21
[6] Zhou W, Yamaguchi T, Kikuchi K, Nomura N and Kawasaki A 2017 Effectively enhanced load transfer by interfacial reactions in multi-walled carbon nanotube reinforced Al matrix composites Acta. Mater. 125 369–76
[7] Lu Y, Chen J, Wang R, Xu P, Zhang X, Gao B, Guo C and Yang G 2019 Bio-inspired Cu-alginate to smartly enhance safety performance and the thermal decomposition of ammonium perchlorate Appl. Surf. Sci. 470 269–75
[8] Tang P, Li W, Zhao Y, Wang K, Li W and Zhan F 2017 Influence of strontium and lanthanum simultaneous addition on microstructure and mechanical properties of the secondary Al–Si–Cu–Fe alloy J. Rare. Earth. 35 485–93
[9] Chen Y, Cheng M, Song H, Zhang S, Liu J and Zhu Y 2014 Effects of lanthanum addition on microstructure and mechanical properties of as-cast pure copper J. Rare. Earth. 32 1056–63
[10] Gu D, Shen Y, Zhao L, Xiao J, Wu P and Zhu Y 2007 Effect of rare earth oxide addition on microstructures of ultra-fine WC–Co particulate reinforced Cu matrix composites prepared by direct laser sintering Mat. Sci. Eng. A 445–446 316–22
[11] Xue J, Wang J, Han Y, Li P and Sun B 2011 Effects of CeO$_2$ additive on the microstructure and mechanical properties of in situ TiB$_2$/Al composite J. Alloys. Compd. 509 1573–8

12
Zhuo H, Tang J and Ye N 2013 A novel approach for strengthening Cu–Y2O3 composites by in situ reaction at liquidus temperature Mater. Sci. Eng. A 584 1–6
Shi J, Bingqiu Z, Zhen Z and Xin J 2006 Application of lanthanum in high strength and high conductivity copper alloys J. Rare. Earth. 24 385–8
Deng L, Zhou B, Yang H, Jiang X, Jiang B and Zhang X 2015 Roles of minor rare-earth elements addition in formation and properties of Cu–Zr–Al bulk metallic glasses J. Alloys. Compd. 632 429–34
Bai G, Liu Z, Lin J, Yu Z, Hu Y and Wen C 2016 Effects of the addition of lanthanum and ultrasonic stirring on the microstructure and mechanical properties of the in situ Mg3Si alloy composites Mater. Design. 90 424–32
Golmakanivooan S and Mahmudi R 2011 Comparison of the effects of La- and Ce-rich rare earth additions on the microstructure, creep resistance, and high-temperature mechanical properties of Mg–6Zn–3Cu cast alloy Mat. Sci. Eng. A 528 5228–33
Inoue A, Yamaguchi H, Zhang T and Masumoto T 1990 Al–La–Cu amorphous alloys with a wide supercooled liquid region Mater. Trans. 32 104–9
Ma X, Qian Y and Yoshiida F 2002 Effect of La on the Cu–Sn intermetallic compound (IMC) growth and solder joint reliability J. Alloys. Compd. 334 224–7
Li M, Hao H, Zhang A, Song Y and Zhang X 2012 Effects of Nd on microstructure and mechanical properties of as-cast Mg–8Li–3Al alloy J. Rare. Earth. 30 392–6
Zheng R and Li N 2019 Mechanical properties and electrical conductivity of nano-La2O3 reinforced copper matrix composites fabricated by spark plasma sintering Mater. Res. Express. 6 106527
Zou C, Kang H, Wang W, Chen Z, Li R, Gao X, Li T and Wang T 2016 Effect of La addition on the particle characteristics, mechanical and electrical properties of in situ Cu–TiB2 composites J. Alloys. Compd. 687 312–9
Ngai T L, Zheng W and Li Y 2013 Effect of sintering temperature on the preparation of Cu–Ti3SiC2 metal matrix composite Prog. Nat. Sci.: Mater. Int. 23 70–6
Liu Q, He X-B, Ren S-B, Liu T-T, Kang Q-P and Qu X-H 2013 Fabrication and thermal conductivity of copper matrix composites reinforced with Mo2C or TiC coated graphite fibers Mater. Res. Bull. 48 4811–7
Ružić J, Stacić J, Rajković V and Bezić D 2014 Synthesis, microstructure and mechanical properties of ZrB2 nano and microparticle reinforced copper matrix composite by in situ processings Materials & Design. (1980–2015) 62 409–15
Chokshi A H, Rosen A, Karch J and Gleiter H 1989 On the validity of the hall-perch relationship in nanocrystalline materials Scripta Metall. 23 1679–84
Agarwala M, Bourel D, Beaman J, Marcus H and Barlow J 1995 Direct selective laser sintering of metals Rapid. Prototyping J. 1 26–36
Zhang K, Gao C, He F and Lin Y 2018 The role of rare Earth lanthanum oxide in polymeric matrix brake composites to replace copper Polymers. 10 1027
Fu J, Yin S, Dong Z, Wang Y and Liu Y 2017 Effect of La2O3 on microstructure and properties of Cu20Fe80 alloy by microwave sintering Mat. Sci. Eng. 207 012014
Chu K and Jia C 2014 Enhanced strength in bulk graphene–copper composites Phys. Status. Solidi (a) 211 184–90
Sinha V and Spowart J E 2012 Influence of interfacial carbide layer characteristics on thermal properties of copper–diamond composites J. Mater. Sci. 48 1330–41
Han Y, Duan H, Lu W, Wang L and Zhang D 2015 Fabrication and characterization of laminated Ti–(TiB + La2O3)/Ti composite Prog. Nat. Sci.: Mater. Int. 25 453–9
Zhou W, Yamamoto G, Fan Y, Kwon H, Hashida T and Kawasaki A 2016 In-situ characterization of interfacial shear strength in multi-walled carbon nanotube reinforced aluminum matrix composites Carbon 106 37–47
Kessman A J, Zhang J, Vasudevan S, Lou J and Sheldon B W 2015 Carbon nanotube pullout, interfacial properties, and toughening in ceramic nanocomposites: mechanistic insights from single fiber pullout analysis Adv. Mater. Interfaces. 2 1400110
Chu K, Wang F, Wang X-H and Huang D-J 2018 Anisotropic mechanical properties of graphene/copper composites with aligned graphene Mat. Sci. Eng. A 713 269–77