**Rare Metal Materials and Engineering**
Volume 47, Issue 8, August 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

**Cite this article as:** Rare Metal Materials and Engineering, 2018, 47(8): 2312-2317.

ARTICLE

# Effects of Hot-rolling Reduction on Microstructure and Mechanical Properties of GNPs/Ti Composites

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**Abstract:** Graphene nanoplatelets (GNPs)/Ti composites were fabricated by spark plasma sintering (SPS) and hot-rolling. This work was focused on the effects of rolling reduction on microstructure and mechanical properties of GNPs/Ti composites. The SEM microstructure results show that matrix grains are gradually elongated and the amount of GNPs along the rolling direction rises with the increase of rolling reduction. The tensile test results indicate that the ultimate tensile strength and fracture elongation of the GNPs/Ti composites increase with the increase of rolling reduction. The ultimate tensile strength of the composites at 60% rolling reduction is 680 MPa, which is increased by 33% compared with pure Ti. Hot-rolling process can relieve defects and lead to GNPs aligned along the rolling direction, which improves the tensile property.

**Key words:** GNPs/Ti composites; rolling reduction; microstructure; mechanical property

With the rapid development of composite materials, Ti matrix composites have been drawing great attention because of their low density, high specific strength, high specific modulus and high temperature strength [1,2]. Therefore, they have been used in aerospace and automobile fields [1-3]. However, many problems restricting the further applications of Ti matrix composites, such as unstable fabrication processes and dispersion of the reinforcements, have not been well resolved[4]. Due to the poor plasticity of the composites, thermal deformation technologies have been generally used for the composite forming[5].

Different micron-scaled reinforcements generated by the in-situ reactions between the external elements and titanium matrix including TiC particles and TiB whiskers were investigated[6-8]. These reinforcements are uniformly dispersed in the matrix, so that Ti matrix composites have good mechanical properties in room temperature and high temperature environment [9-12]. Several researches present nano-scaled materials such as carbon nanotubes (CNTs) as novel reinforcements for the Ti matrix composites and TiC phase was in-situ formed during the production [13,14]. Graphene, as the perfect two-dimensional lattice of sp2-bonded carbon atoms, has attracted extensive attention due to its extraordinary mechanical properties and physical properties[15]. In terms of elastic modulus, TiC particles are only 550 GPa, while the graphene is 1 TPa with high fracture strength (125 GPa)[16]. GNPs composed of a few graphene layers possess properties similar to that of single-layer graphene but are much easier to produce and handle[17]. Due to the excellent properties, GNPs are regarded as the perfect reinforcement to the metal matrix composites. Compared with other micron-scaled reinforcements, GNPs are easy to aggregate due to their specific surface area and high surface energy. The main challenge is how to disperse the GNPs more uniformly in the Ti matrix and to form a good interfacial bonding[18,19]. Owing to the clustering of the reinforcements, hot-rolling has considerable potential.

The primary objective of this work is to improve the dispersion of GNPs in the Ti matrix and the bonding between GNPs and Ti matrix using hot-rolling process. Here, we introduced a favorable route to produce GNPs/Ti composites with excellent performances. Firstly, the mixed powders were fabricated using ultrasonic dispersion and ball milling. Then, the mixed powders were sintered by spark plasma sintering

Received date: August 17, 2017
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(SPS) process [20]. Finally, the as-sintered samples were obtained to hot-rolling with different reductions. Further, the effects of rolling reduction on microstructure and mechanical properties of the composite were investigated.

## 1 Experiment

### 1.1 Raw materials

A type of Ti powders (0~45 μm diameter, provided by Chengdu Excellent Material Technology Corporation) was employed as starting matrix material. It can be seen that the Ti powders are spherical (Fig.1a). GNPs (2~5 nm thickness, 6~11 layers and 10~20 nm length) were prepared by an improved Hummer's method. Fig.1b shows the scanning electron microscopy (SEM) image of GNPs which were sheets, wrapped together layer by layer and agglomerated severely. Fig.1c shows the transmission electron microscopy (TEM) image of GNPs which have a large specific surface area and two-dimensional high aspect ratio sheet geometry.

### 1.2 Powder treatment and composites preforming

GNPs (0.035 g) were exfoliated by ultrasonic dispersion in ethanol. Then GNPs solution was added into the nylon jar which was placed with Ti powders and $ZrO_2$ ceramic balls (3 mm diameter, 175 g). The ball-to-powder mass ratio was 5:1 and the mass ratio of Ti powders to GNPs was 99.9:0.1. Planetary ball milling was performed at a rotation speed of 350 r/min for 2.5 h. The ball milled mixture was filtered and dried at 80 °C for 12 h to obtain the mixed powder.

The mixed powder was containerized in an alloy die and then consolidated using the SPS technique at 873 K, 300 MPa for 5 min in a vacuum of 1 Pa. The sintered samples were cylindrical billets with a diameter of 25 mm and a height of 15 mm. For the purpose of comparison, Ti powders were prepared under the same conditions.

### 1.3 GNPs alignment by hot-rolling

The surface of the sintered samples was machined to remove the surface reaction layer and defects. To align the GNPs in the Ti matrix, the samples were heated to a pre-determined temperature of 1223 K, and rolling was conducted with a 20% reduction per pass. Table 1 shows the number of rolling passes and different rolling reductions. The as-sintered samples using Ti powders were rolled with 3 passes of 60% reduction under the same conditions. A schematic illustration of hot-rolling process is shown in Fig.2.

### 1.4 Characterization of the composites

The GNPs distributions in the matrix under different rolling reductions were examined using scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, Quanta 3D 200). The density of GNPs/Ti composites was tested by Archimedes method.

Tensile specimens (a gauge length of 10 mm, a width of 3.2 mm, and a thickness of 1 mm) were machined from the rolled composites parallel to the rolling direction. Tensile tests were conducted at a strain rate of $1\times10^{-3}$ $s^{-1}$ at room temperature using an Instron 5848 microtester to obtain engineering stress-strain curves. At least three specimens were tested for each

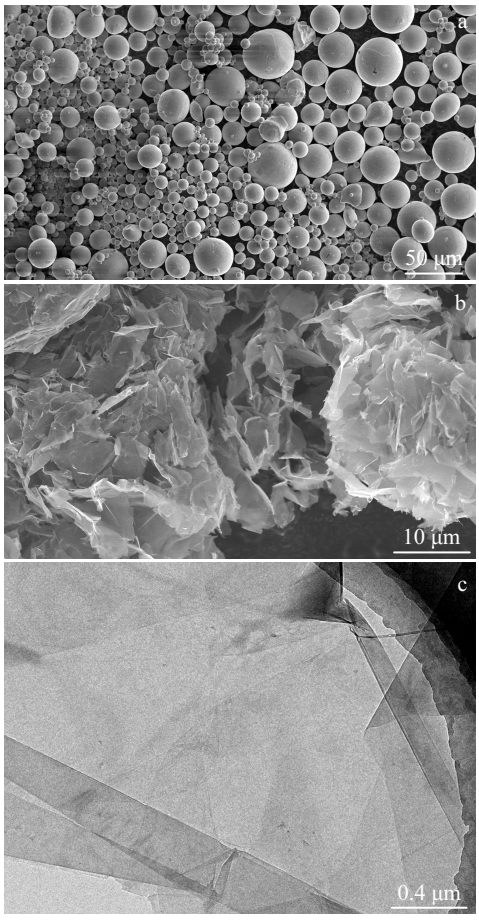


Fig.1 SEM (a, b) and TEM (c) images of initial powder: (a) Ti powder and (b, c) GNPs powder

**Table 1 Rolling pass and reduction**

| Specimen | GNPs content/wt% | Number of rolling passes | Reduction/ % |
|---|---|---|---|
| Ti1 | 0 | 0 | 0 |
| Ti2 | 0 | 3 | 60 |
| TMCs1 | 0.1 | 1 | 20 |
| TMCs2 | 0.1 | 2 | 40 |
| TMCs3 | 0.1 | 3 | 60 |

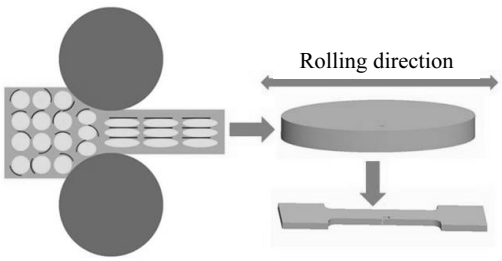


Fig.2 Diagram of the rolling process and sampling

composite. For the purpose of comparison, the tensile tests on the pure Ti were conducted under the same conditions.

## 2 Results and Discussion

### 2.1 Archimedes density

The results of density are shown in Table 2. It can be seen that with the increase of rolling reduction, the density and the relative density of the composite increase. It indicates that the defects of the composite such as pores are relieved with the increase of rolling reduction.

### 2.2 Microstructures

Morphologies of ball-milled powders and the sintered samples are shown in Fig.3. Exfoliated GNPs are observed on the surface of the Ti powder, where GNPs are marked by arrows in Fig.3a. Fig.3b displays magnified images of the ball-milled powder, where GNPs are thin enough to transmit the electron beam so the Ti powder underneath the GNPs can be seen[11]. The spherical shape of the Ti powder keeps well. GNPs are distributed uniformly with original structure; however, there are still agglomeration phenomenon of GNPs in local area. Most of the GNPs are attached to the surface of the Ti powders with the size of 5~10 μm. Compared with the GNPs in Fig. 1b, it can be seen that the GNPs are peeled off after ultrasonic dispersion and ball milling. GNPs are broken and the size of GNPs declines. Therefore, the agglomerated GNPs can be separated by ultrasonic dispersion. The ball milling method can make the GNPs adhere closely to the Ti powders and disperse well.

**Table 2 Archimedes density of the composites**

| Specimen | Arch. density/ g·cm$^{-3}$ | Theoretical density/g·cm$^{-3}$ | Relative density/% |
|---|---|---|---|
| Ti1 | 4.435 | 4.510 | 98.34 |
| Ti2 | 4.502 | 4.510 | 99.82 |
| TMCs1 | 4.381 | 4.497 | 97.42 |
| TMCs2 | 4.422 | 4.497 | 98.33 |
| TMCs3 | 4.454 | 4.497 | 99.05 |

SEM images of the sintered sample are shown in Fig.3c and 3d. Microstructural characterization shows good bonding between Ti particles, and GNPs exist at the boundaries of the matrix (Fig.3c). After SPS sintering, the GNPs/Ti composites are compacted, the GNPs are mainly distributed between the particles (Fig.3d). There are big pores between the GNPs and the Ti particles.

Fig.4 is the microstructure of the GNPs/Ti composites with different rolling reductions. It can be seen that no GNPs clusters are observed under SEM in the composites.

Compared with Fig.3c, the microstructures of GNPs/Ti composites are obviously changed after rolling deformation. Two phenomena could be observed. The first is that pores become small after hot-rolling. Secondly, GNPs are generally aligned along the rolling direction and uniformly dispersed in the matrix. This is attributed to the plastic deformation during hot-rolling. At the stage of ball milling, the GNPs are peeled off and broken. The broken GNPs are able to flow with the plastic deformation of the composites during hot-rolling.

At 20% rolling reduction, each grain is approximately equiaxial (Fig.4a). With an increase of rolling reduction to 40%, the microstructure continues to show disorganized GNPs in the matrix (Fig.4c). Fig.4f shows that the GNPs are aligned along the rolling reduction and the grains are elongated.

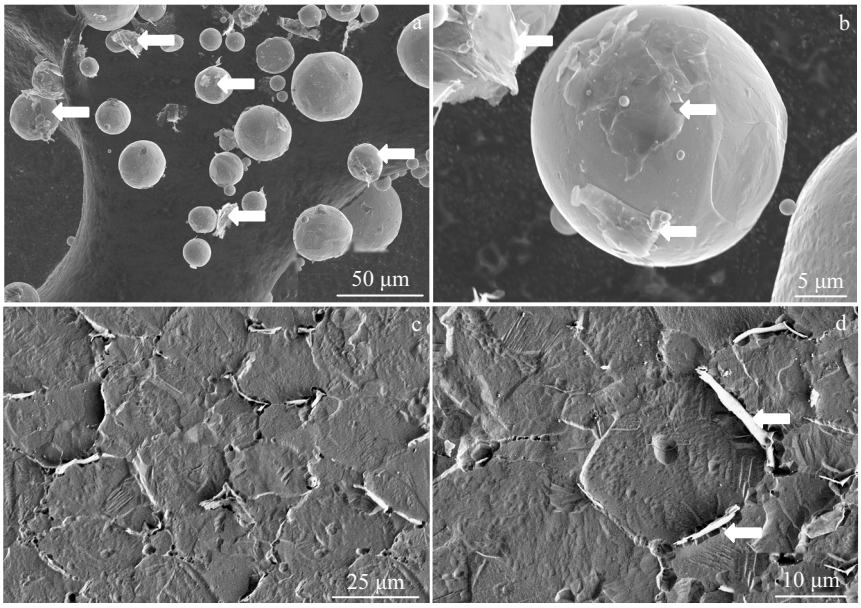


Fig.3 SEM images of the mixed powder and sintered composite: (a, b) mixed powder and (c, d) sintered GNPs/Ti composite

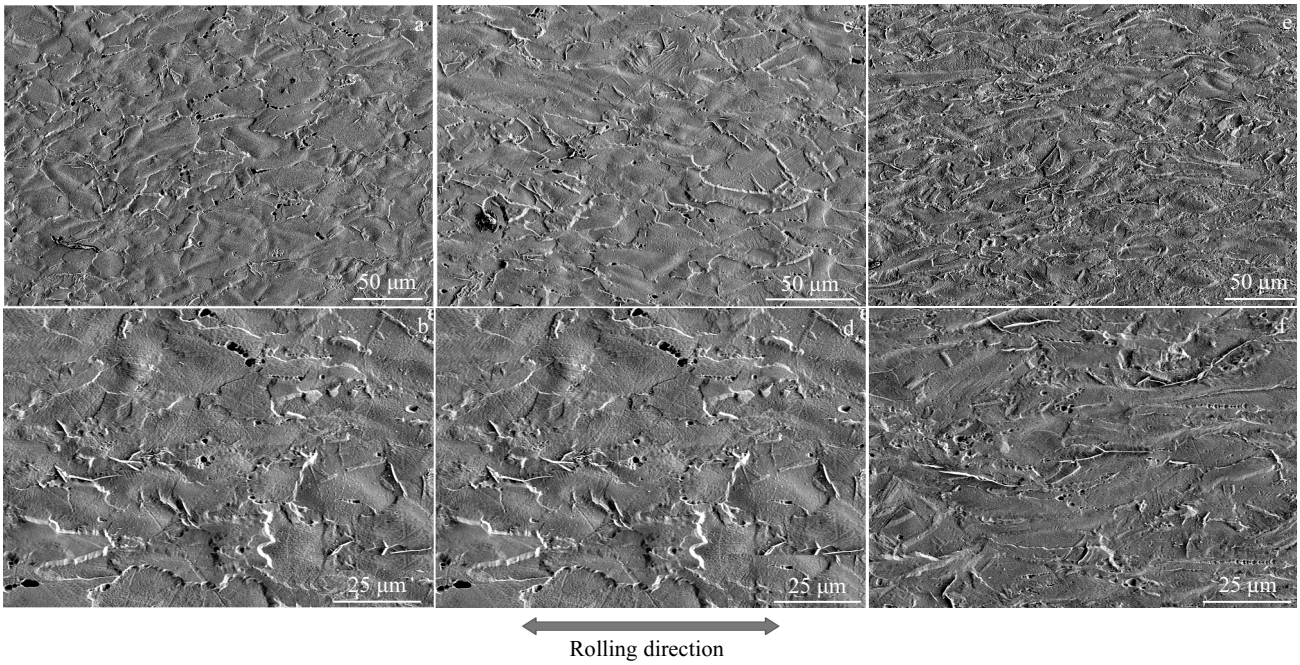


Fig.4 SEM images of the GNPs/Ti composites at different rolling reductions: (a, b) 20%, (c, d) 40%, and (e, f) 60%

### 2.3 Fracture surfaces

Fig.5 shows the SEM images of tensile fracture of GNPs/Ti composites at different rolling reductions. The fracture morphology of dimples and tear ridges which exhibit the ductile fracture can be seen in Fig.5a. With the increase of rolling reduction, the dimple is much denser, shallower and smaller (Fig. 5a~5c). Fig. 5e shows the characteristic peaks of C and Ti elements at point 1 in Fig. 5d. The contents of Ti and C atoms at this point is presented in Table 3. It indicates that the GNPs may insert into the Ti matrix. Fractured GNPs can be observed in cracks (shown in Fig. 5d) which indicates that they effectively undertake the load transferred from the matrix.

### 2.4 Mechanical properties

Tensile tests were carried out to further analyze the effect of hot-rolling reduction degree on mechanical property of the composites (shown in Table 4 and Fig.6). It can be seen that the ultimate tensile strength of GNPs/Ti composites increases with the rise of rolling reduction. The ultimate tensile strength

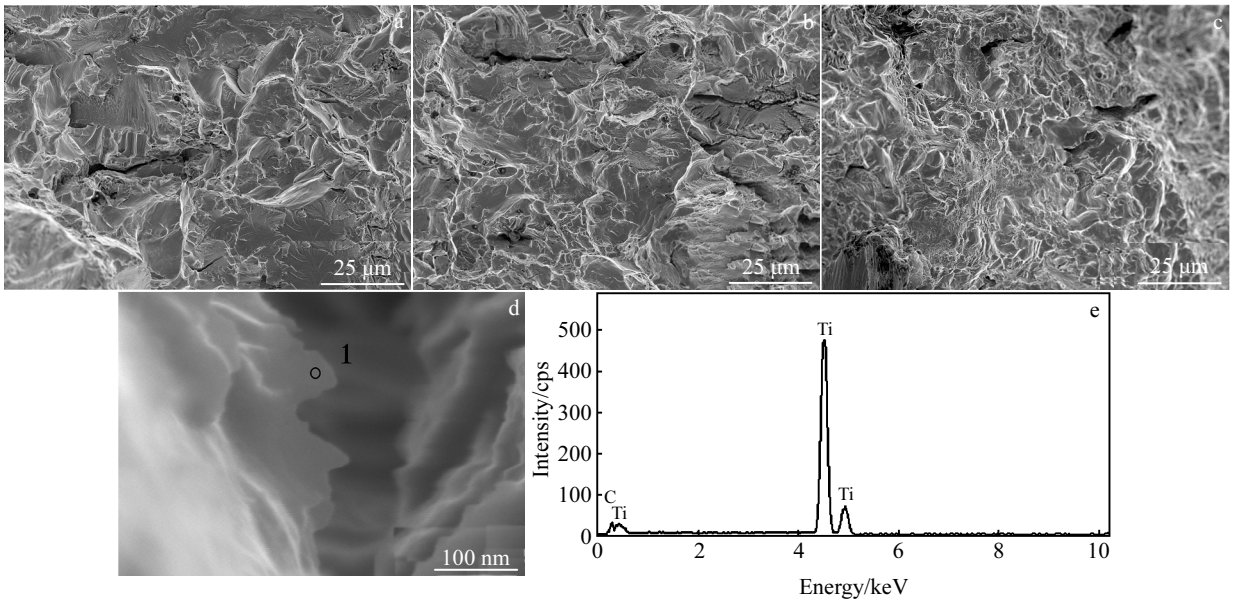


Fig.5 SEM fracture surfaces (a~c) and EDS spectrum of point 1 (d, e) for GNPs/Ti composite: (a) 20%, (b) 40%, and (c) 60%

**Table 3 Element content of point 1 in Fig.5d**

| Element | wt% | at% |
|---|---|---|
| C | 6 | 20.28 |
| Ti | 94 | 79.72 |

**Table 4 Tensile properties of the composites**

| Specimen | GNPs/wt% | Reduction/% | $\sigma_b$/MPa | $\delta$/% |
|---|---|---|---|---|
| Ti2 | 0 | 60 | 513 | 28.4 |
| TMCs1 | 0.1 | 20 | 640 | 15.6 |
| TMCs2 | 0.1 | 40 | 660 | 18.6 |
| TMCs3 | 0.1 | 60 | 680 | 24.6 |

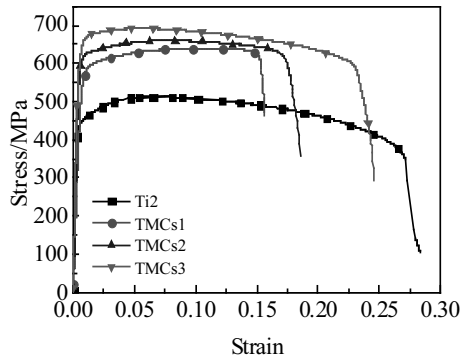


Fig.6 Room temperature tensile properties of specimens hot-rolled at different reductions

of the composites at 60% rolling reduction reaches 680 MPa, which demonstrated 33% higher than pure Ti. The strain increased from 15.6% to 24.6% with increasing the hot-rolling reduction from 20% to 60%.

Based on the fracture strength of GNPs and the alignment of GNPs in the tensile direction, an improvement in tensile strength as high as 680 MPa can be theoretically expected from the addition of 0.1 wt% GNPs into the titanium matrix. With the rise of the rolling reduction, the amount of pores between the GNPs and the Ti particles gradually decreases. When the GNPs/Ti composite is loaded, the titanium matrix is strained and then the strained matrix may transfer the load to GNPs by means of shear stresses along the reinforcement-matrix interface. The microstructure analysis reveals that the shrinkage and decrease of pores and grain refinement contribute to the improvement in the tensile strength of GNPs/Ti composites. Additionally, GNPs can effectively prevent grain growth to exhibit the grain refinement effect. Despite load transfer from matrix to GNPs and the grain refinement, texture strengthening after hot-rolling plays an important role in mechanical performance of GNPs/Ti composites [21,22]. Therefore, the shrinkage of pores, load transfer from matrix to GNPs, grain refinement and texture strengthening are considered as the main strengthening mechanisms in this study.

Compared with pure Ti, the plasticity of GNPs/Ti composites become bad. The plastic deformation of the matrix is inhibited by the GNPs at the grain boundaries which makes the deformation difficult coordinated. With the rise of rolling deformation, the defects of the composites are relieved, the pores close, the grains of the composites strain and the deformation energy is uniformly dispersed in each grain, thereby enhancing the plasticity of the composite. These results demonstrate that GNPs have huge potential as the ideal reinforcement in titanium matrix composites.

## 3 Conclusions

1) GNPs/Ti composites are fabricated by SPS and hot-rolling. With the increase of rolling reduction, the aspect ratio of the matrix grain increases, and GNPs are generally aligned along the rolling direction.

2) The ultimate tensile strength of GNPs/Ti composites increases with the increase of rolling deformation, and the ultimate tensile strength reaches 680 MPa (at 60% rolling reduction), which is 33% higher than that of pure Ti. The tensile property of the composites is improved by hot-rolling.

3) The original structure of GNPs can be retained by the preparation to enhance the mechanical properties of the composites.

## References

1 Abkowitz S, Fisher H. *Journal of the Minerals Metals and Materials Society*[J], 2004, 56(5): 37
2 Saito T, Takamiya H, Furuta T. *Materials Science and Engineering A*[J], 1998, 243(1-2): 273
3 Kuang Da, Hu Wenbin. *Journal of Inorganic Materials*[J], 2013, 28(3): 235 (in Chinese)
4 Qu S J, Geng L, Meng Q C *et al. Rare Metals*[J], 2005, 24(1): 95
5 Xu S C, Wang L D, Zhao P T *et al. Materials Science and Engineering A*[J], 2012, 550: 146
6 Ma Fengcang, Liu Ping, Liu Xinkuan. *Shanghai Nonferrous Metal*[J], 2016, 37(1): 9 (in Chinese)
7 Shang J L, Li B S, Guo J J *et al*. *Transactions of Nonferrous Metals Society of China*[J], 2003, 13(2): 315
8 Guo X L, Wang L Q, Qin J N *et al*. *Transactions of Nonferrous Metals Society of China*[J], 2014, 24(6): 1737
9 Ni D R, Geng L, Zhang J *et al*. *Materials Science and Engineering A*[J], 2008, 478(1-2): 291
10 Liu Z Y, Xiao B L, Wang W G *et al*. *Carbon*[J], 2013, 62(5): 35
11 Shin S E, Choi H J, Shin J H *et al*. *Carbon*[J], 2015, 82: 143
12 Yan Shaojiu, Yang Cheng, Hong Qihu. *Journal of Materials Engineering*[J], 2014(4): 1 (in Chinese)
13 Montealegre Melendez I. *Composites Science and Technology* [J], 2011, 71(8): 1154
14 Li S F, Sun B, Imai H *et al*. *Composites: Part A* [J], 2015, 6(2): 16
15 Novoselov K S, Geim A, Morozov S V *et al*. *Science*[J], 2004, 306(5296): 666
16 Lee C, Wei, X D, Kysar J W *et al*. *Science*[J], 2008, 321(5887):

385
17 Wang J Y, Li Z Q, Fan G L *et al*. *Scripta Materialia*[J], 2012, 66(8): 594
18 Zhang Dandan, Zhan Zaiji. *Journal of Materials Engineering*[J], 2016, 44(5): 112 (in Chinese)
19 Zhang Yu, Song Meihui, Zhang Xiaochen *et al. Heilongjiang Science*[J], 2015, 6(2): 16 (in Chinese)
20 Zhang Z H, Liu Z F, Lu J F *et al*. *Scripta Materialia*[J], 2014, 81(11): 56
21 Chen B, Li S F, Imai H *et al. Composite Science Technology*[J], 2015, 133: 1
22 Mu X N, Zhang H M, Cai H N *et al. Materials Science and Engineering A*[J], 2017, 687: 164

# 轧制变形量对 GNPs/Ti 复合材料组织与性能的影响

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**摘　要**：采用放电等离子烧结技术(SPS)和热轧制备了石墨烯/钛基复合材料（GNPs/Ti）。重点研究了轧制变形量对 GNPs/Ti 复合材料的显微组织及力学性能的影响规律。采用扫描电镜观察不同变形量后的显微组织，结果显示，随着轧制变形量的增加，基体晶粒长径比增大，石墨烯取向性提高。拉伸结果表明，GNPs/Ti 复合材料的抗拉强度和断后伸长率随着变形量的增加而增加，在变形 60%时，最大抗拉强度达到 680 MPa，相比纯钛提高了 33%。采用轧制工艺可以使 GNPs/Ti 复合材料孔洞减少、GNPs 分布具有取向性，从而提高材料的力学性能。

**关键词**：石墨烯/钛基复合材料；轧制变形量；显微组织；力学性能

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