

# Anisotropic Fracture Toughness and Microstructure of Graphene-Reinforced TiC/Si<sub>3</sub>N<sub>4</sub> Composite

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## Abstract

Using the hot pressing sintering process, graphene-platelets (GPLs)-reinforced TiC/Si<sub>3</sub>N<sub>4</sub> composite (GPLs/TiC/Si<sub>3</sub>N<sub>4</sub>) was prepared with the aim of improving its fracture toughness. Microstructure analysis shows that the pressure applied during the hot pressing sintering process leads to the orientational distribution of GPLs perpendicular to the pressing direction in the GPLs/TiC/Si<sub>3</sub>N<sub>4</sub> composite. With the single-edge notched beam method, the fracture toughness of GPLs/TiC/Si<sub>3</sub>N<sub>4</sub> was measured in the hot pressing direction (HPD) and perpendicular to the hot pressing direction (PHPD). The fracture toughness of the composites in HPD is higher than that in PHPD. The maximum fracture toughness of 9.6 MPa · m<sup>1/2</sup> in HPD was achieved for the composite containing 1 wt% GPLs, which was approximately 31.5 % higher than that of 7.3 MPa · m<sup>1/2</sup> in PHPD. Raman spectra showed that the defect in PHPD was larger than that in HPD. The Raman intensity of the composite in HPD is higher than that in PHPD. The toughening mechanisms include crack deflection, graphene bridging and the pull-out of GPLs, which were observed and discussed.

*Keywords:* Graphene, orientation, fracture toughness, microstructure

## I. Introduction

Silicon nitride ceramics have superior mechanical properties such as high hardness, high strength and excellent wear resistance, which make them ideal candidate materials for gas turbine engine parts, bearing balls and cutting tools <sup>1,2</sup>. However, the brittleness of silicon nitride is one of the most crucial problems in their application. In order to improve the toughness of silicon nitride materials, a variety of reinforcing materials such as CNT, SiC<sub>w</sub>, SiC, BN-NTs and TiC have been incorporated to develop silicon-nitride-based composites. For example, Tian *et al.* <sup>3</sup> prepared TiC/Si<sub>3</sub>N<sub>4</sub> composites and demonstrated that the toughness of composites could be improved with the addition of TiC. Chen *et al.* <sup>4</sup> reported an increase in fracture toughness of 40 % in Si<sub>3</sub>N<sub>4</sub> materials reinforced with 1.5 wt% BNNTs.

In recent years, graphene has attracted tremendous attention owing to its extreme mechanical properties <sup>5</sup>. The literature <sup>6–10</sup> has reported that the addition of graphene can significantly improve the fracture toughness of ceramic composites. With the addition of 1 wt% GPLs <sup>6</sup>, sintered in a hot pressing process at 1750 °C for 60 min under 25 MPa, the fracture toughness of Si<sub>3</sub>N<sub>4</sub> composite was up to 8.6 MPa · m<sup>1/2</sup>. Walker *et al.* <sup>7</sup> exhibited the improved fracture toughness of Si<sub>3</sub>N<sub>4</sub>/GPLs composite and the highest value was 6.6 MPa · m<sup>1/2</sup>. Liu *et al.* <sup>8</sup> prepared

GPLs-reinforced Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> composites with the SPS sintering method and achieved a 40 % increase in fracture toughness.

The pressure applied during the hot pressing sintering process leads to the directional distribution of graphene, which produces the anisotropy of the thermal conductivity and conductive property of the composite in the two directions (HPD and PHPD) <sup>11</sup>. Miranzo *et al.* <sup>12</sup> found that the addition of carbon nanostructures (carbon nanotubes and graphene) leads to anisotropic thermal conductivity of silicon-nitride-based composite. Seiner *et al.* <sup>13</sup> reported that silicon nitride composites have an anisotropic Young's modulus and shear modulus with the addition of graphene. However, anisotropic fracture toughness of graphene-reinforced ceramic materials has been the subject of only limited research up to now.

In this study, GPLs/TiC/Si<sub>3</sub>N<sub>4</sub> composites were prepared using the hot pressing sintering process. The influence of the addition of GPLs on the fracture toughness of the composites in both directions was researched. Furthermore, the microstructure and toughening mechanisms of the composite were observed and discussed.

## II. Experimental Procedure

### (1) Material preparation

Commercially available α-Si<sub>3</sub>N<sub>4</sub> powders with average grain size of approximately 0.5 μm and purity > 99 % (Nanjing Guanye Chemical Co, Ltd, China), TiC pow-

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der with average grain size of approximately  $0.5\ \mu\text{m}$  and purity  $>99.5\%$  (Shanghai Chaowei Nanotechnology Co, Ltd, China), graphene with approximate thickness  $10\ \text{nm}$ , diameter of approximately  $5\ \mu\text{m}$  and purity  $>95\%$  (Nanjing Xianfeng Nanomaterials Technology Co, Ltd, China) were used as the starting materials.  $\text{MgO}$  (Sinopharm Chemical Reagent Co, Ltd, Shanghai, China),  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  (Shanghai Chaowei Nanotechnology Co, Ltd, China) were used as sintering aids to promote the densification of GPLs/ $\text{TiC}/\text{Si}_3\text{N}_4$  composites. The compositions of the GPLs/ $\text{TiC}/\text{Si}_3\text{N}_4$  composites are listed in Table 1. The samples are written as  $\text{STG}_x$ , where  $x$  denotes the amount of GPLs.

**Table 1:** Compositions of GPLs/ $\text{TiC}/\text{Si}_3\text{N}_4$  composites (wt%).

| samples             | $\text{Si}_3\text{N}_4$ | TiC | GPLs | $\text{Al}_2\text{O}_3$ | $\text{Y}_2\text{O}_3$ | MgO |
|---------------------|-------------------------|-----|------|-------------------------|------------------------|-----|
| $\text{STG}_0$      | 77.5                    | 15  | 0    | 2                       | 5                      | 0.5 |
| $\text{STG}_{0.5}$  | 77                      | 15  | 0.5  | 2                       | 5                      | 0.5 |
| $\text{STG}_{0.75}$ | 76.75                   | 15  | 0.75 | 2                       | 5                      | 0.5 |
| $\text{STG}_1$      | 76.5                    | 15  | 1    | 2                       | 5                      | 0.5 |
| $\text{STG}_{1.5}$  | 76                      | 15  | 1.5  | 2                       | 5                      | 0.5 |

The surfactant polyvinylpyrrolidone (PVP) and isopropyl alcohol were used as the dispersant and dispersing medium, respectively.  $\text{Si}_3\text{N}_4$  and TiC powders were dispersed in isopropyl alcohol with the sintering aids, assisted by mechanical stirring and ultrasonic vibration. The mixed solution was then milled for 42 h. After that, GPLs were dispersed in isopropyl alcohol with PVP (PVP amount equivalent to GPLs), assisted by ultrasonic vibration. The dispersed GPLs solution was added to the milled solution and milling was then continued for 6 h. The slurry was vacuum-dried at  $100\ ^\circ\text{C}$  for 24 h and then sieved. The dried mixtures were sintered to discs measuring  $42\ \text{mm}$  in diameter and  $5\ \text{mm}$  in thickness at  $1700\ ^\circ\text{C}$  for 60 min under a uniaxial pressure of  $25\ \text{MPa}$ .

## (2) Characterization

The sintered materials were cut with a diamond wheel into bars with the dimensions of  $3\ \text{mm} \times 3\ \text{mm} \times 30\ \text{mm}$ . The bars were then ground and polished to an average surface roughness less than  $0.1\ \mu\text{m}$ . Fracture toughness was measured using the single-edge notched beam method on a CMT5105 electromechanical universal testing machine (Shenzhen SANS Testing Machine Co., Ltd., China) with a span of  $20\ \text{mm}$  at a speed of  $0.05\ \text{mm}/\text{min}$ <sup>4</sup>. A notch with the depth of  $1.5\ \text{mm}$  and width of  $0.3\ \text{mm}$  was introduced in the middle of each specimen using a thin diamond blade. The fracture toughness of the specimen was measured in the two directions of HPD and PHPD, which can be seen in Fig. 1. The data of the fracture toughness were calculated as the average value of six samples for each composition. Raman spectroscopy (LabRAM HR800, HORIBA JY, France) was performed for GPLs phase identification. In order to reveal the toughening mechanism of graphene in the composite, the crack was introduced with an in-

dentation tester (HVS-50, China) at loads of  $196\ \text{N}$  and a holding time of  $15\ \text{s}$ . The phase composition of the sintered materials was checked using x-ray diffraction (XRD) (D8-ADVANCE, Bruker AXS, Germany) in the  $2\theta$  angle range of  $15\text{--}80^\circ$ . Microstructure characterization of polished surfaces and fractographic observations were performed with a field emission scanning electron microscope (SEM) (SUPRA<sup>TM</sup> 55, Germany).

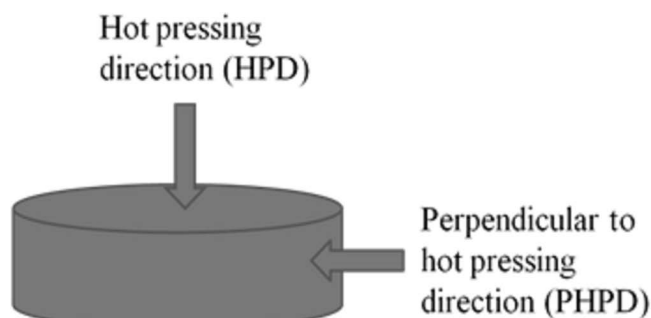


**Fig. 1:** Sketch map of the directions of HPD and PHPD.

## III. Results and Discussion

### (1) Anisotropy of fracture toughness

It is important to note that there are many ways to determine the fracture toughness of ceramic composites, such as the single-edge notched beam method (SENB)<sup>14</sup>, the single-edge V-notch beam method (SEVNB)<sup>15</sup> and Vickers indentation. Strobl *et al.*<sup>16</sup> provided practical guidance for specimen preparation and researched a more precise fracture toughness measurement in brittle materials. The method of fracture toughness using SENB by 3-point or 4-point flexure test is one of the most popular and user-friendly methods<sup>17</sup>. However, compared to SENB and SEVNB, the method of Vickers indentation has rarely given accurate fracture toughness values<sup>18</sup>. Therefore, SENB was used to determine the fracture toughness of composites in this study, and limited by the dimensions of the die, the 3-point flexure test was used.

The fracture toughness of the composites exhibits obvious anisotropy in both directions (Fig. 2). The fracture toughness in HPD is higher than that in PHPD. The fracture toughness in both directions is increased and then decreased with the increase of GPLs content. The highest fracture toughness of the  $\text{STG}_1$  composite in HPD reaches  $9.6\ \text{MPa} \cdot \text{m}^{1/2}$ , with an increase of approximately  $33.3\%$  compared with the corresponding material without GPLs ( $7.2\ \text{MPa} \cdot \text{m}^{1/2}$ ). While the fracture toughness of  $\text{STG}_1$  composite in PHPD is only  $7.3\ \text{MPa} \cdot \text{m}^{1/2}$ . The highest fracture toughness in PHPD reaches  $7.6\ \text{MPa} \cdot \text{m}^{1/2}$  of  $\text{STG}_{0.75}$ , enhanced by approximately  $5.5\%$ . The anisotropic fracture toughness is attributed to the orientation distribution of the GPLs, as shown in Fig. 5. Moreover, the anisotropy of the fracture toughness also changes with the different contents of GPLs. The composite containing  $1\ \text{wt}\%$  GPLs exhibits the highest fracture toughness ( $9.6\ \text{MPa} \cdot \text{m}^{1/2}$ ) in HPD, which is approximately  $31.5\%$  higher than that in PHPD ( $7.3\ \text{MPa} \cdot \text{m}^{1/2}$ ).

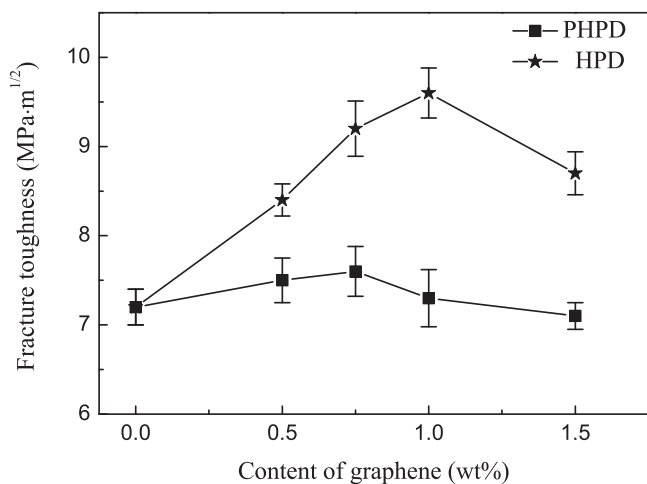


Fig. 2: Fracture toughness of the composite in both directions.

## (2) Phase analysis

Fig. 3 shows the x-ray micrographs of STG<sub>1</sub> composite before and after hot pressing sintering. The diffraction peaks of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> can be seen in Fig. 3(a), while in Fig. 3(b), only  $\beta$ -Si<sub>3</sub>N<sub>4</sub> can be observed. It indicates that the transformation from  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> to  $\beta$ -Si<sub>3</sub>N<sub>4</sub> has been completed. The diffraction peaks of TiC can be observed in Fig. 3(a) and 3(b). It indicates that there is no reaction between Si<sub>3</sub>N<sub>4</sub> and TiC. The main line of the GPLs was not observed because of its minor quantities. Kun *et al.*<sup>19</sup> studied the graphene-reinforced silicon-nitride-based composites and found that the diffraction peaks of graphene cannot be observed with 1 wt% graphene. The identification of GPLs of STG<sub>1</sub> composite was performed based on the Raman spectrum, which can be seen in Fig. 4.

Fig. 4 shows the Raman spectra of STG<sub>1</sub> in HPD and PHPD. From the Fig. 4, it can be seen that the Raman spectra of STG<sub>1</sub> in both directions shows three clear peaks at 1350 cm<sup>-1</sup> (D band), 1570 cm<sup>-1</sup> (G band), and 2700 cm<sup>-1</sup> (2D band)<sup>20</sup>, respectively. These are the typical features of GPLs. In addition, the Raman spectra can be used to research the anisotropy of graphene in ceramics and the ratio of D and G band ( $I_D/I_G$ ) can be used to quantify the defects of graphene<sup>21</sup>. Centeno *et al.*<sup>21</sup> thought that the  $I_D/I_G$  ratio of the edge plane of graphene is larger than that in the basal plane. From Fig. 4, it can be seen that the Raman intensity of composite in HPD is higher than that in PHPD. On the other hand, the  $I_D/I_G$  ratio of HPD is 0.25, which is lower than that in PHPD at about 0.38. It indicates that there are many defects of GPLs in PHPD. Based on the disparity of Raman intensity and  $I_D/I_G$  ratio in both directions, it can be concluded that GPLs exhibited an orientational distribution.

## (3) Microstructure and the orientation of GPLs

Fig. 5 illustrates the fracture surface of STG<sub>1</sub> with the large white arrow in the top-right corner indicating HPD. GPLs (marked by small white arrows) are distributed uniformly in the ceramic matrix with a significant amount of fracture and pull-out of GPLs inserted in the matrix (Fig. 5(a)). In addition, GPLs exhibit a preferred orientation direction, as shown in Fig 5(a). GPLs remain relatively flat and perpendicular to HPD, which can be seen

in Fig. 5(b). Tapasztó *et al.*<sup>11</sup> reported that uniaxial pressure applied during the sintering process leads to the orientational distribution so that more than 80 % of graphene lay within  $\pm 15^\circ$  deviation of the PHPD. The pull-out of GPLs (Fig. 5(a) and 5(b)) can effectively improve the fracture toughness of composites<sup>22</sup>. On the other hand, the directional distribution of GPLs (Fig. 5) results in the anisotropic fracture toughness of GPLs/TiC/Si<sub>3</sub>N<sub>4</sub> composites (Fig. 2).

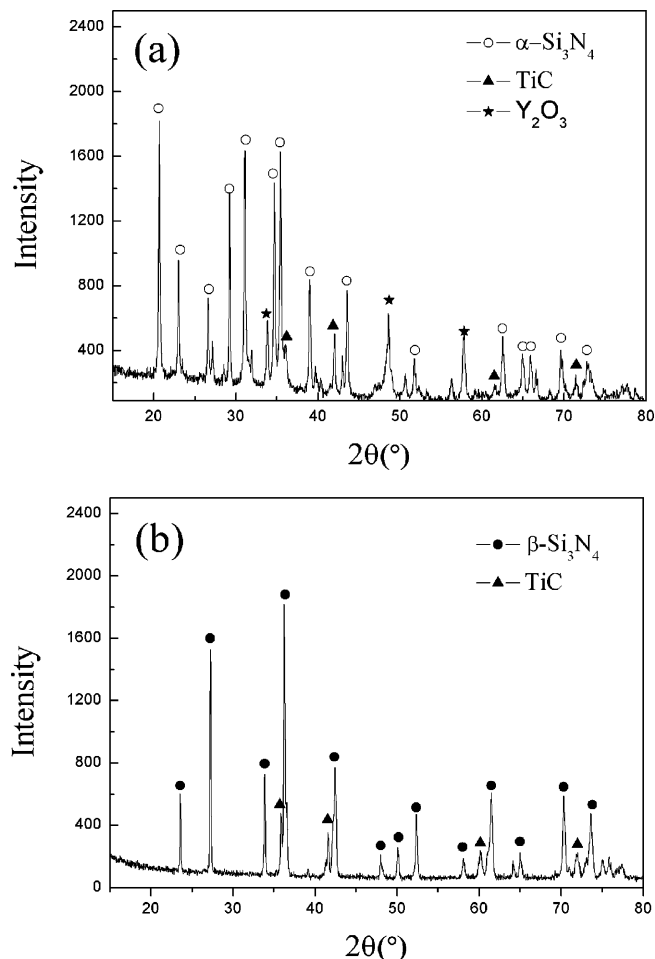


Fig. 3: XRD patterns of STG<sub>1</sub> composite before (a) and after (b) hot pressing sintering.

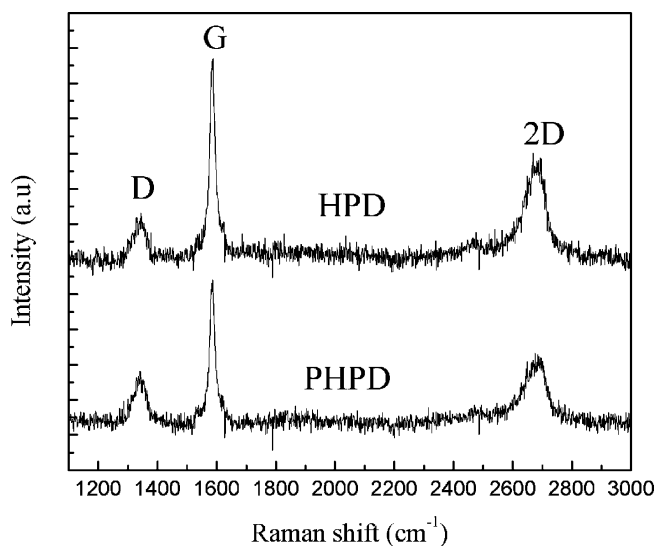


Fig. 4: Raman spectrum of STG<sub>1</sub> composites in both directions.

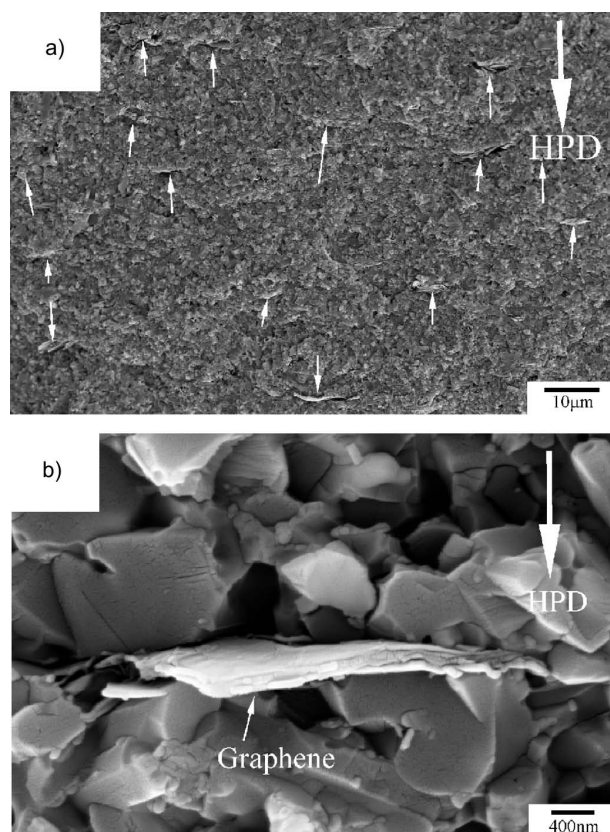


Fig. 5: SEM micrographs of the fracture surface of STG<sub>1</sub> composite.

#### (4) Toughening mechanism

Fig. 6(a) shows the indentation morphology of STG<sub>1</sub> composite. GPLs (black arrows) are perpendicular to HPD and the crack length (approximately 357  $\mu\text{m}$  between A and B) in PHPD is longer than that in HPD (approximately 292  $\mu\text{m}$  between C and D). It indicates that the GPLs in HPD can effectively inhibit crack growth compared to PHPD. Owing to the orientational distribution of GPLs, crack deflection often occurs when the crack propagation meets with GPLs in HPD, as shown in Fig. 6(c). Crack deflection can improve the fracture toughness through a longer path to release energy. However, when the crack growth energy exceeds the limit of GPLs, the crack may penetrate through GPLs (marked 1 in Fig. 6(b)) and continues to extend. The energy needed to penetrate through GPLs is expected to be significantly greater. In addition, graphene has extreme mechanical properties (Young's modulus 1 TPa) and large contact area with matrix. Therefore, the energy needed to pull out GPLs is much greater. Fig. 6(d) shows the sketch map of crack propagation. When the crack extension direction is HPD (Fig. 6(d)), graphene bridging and graphene pull-out can prevent crack expansion<sup>23</sup>. However, crack growth in PHPD is relatively easy, owing to the weak interface of GPLs and substrate material<sup>6</sup>. Therefore, the fracture toughness in HPD was higher than that in PHPD, as shown in Fig. 2.

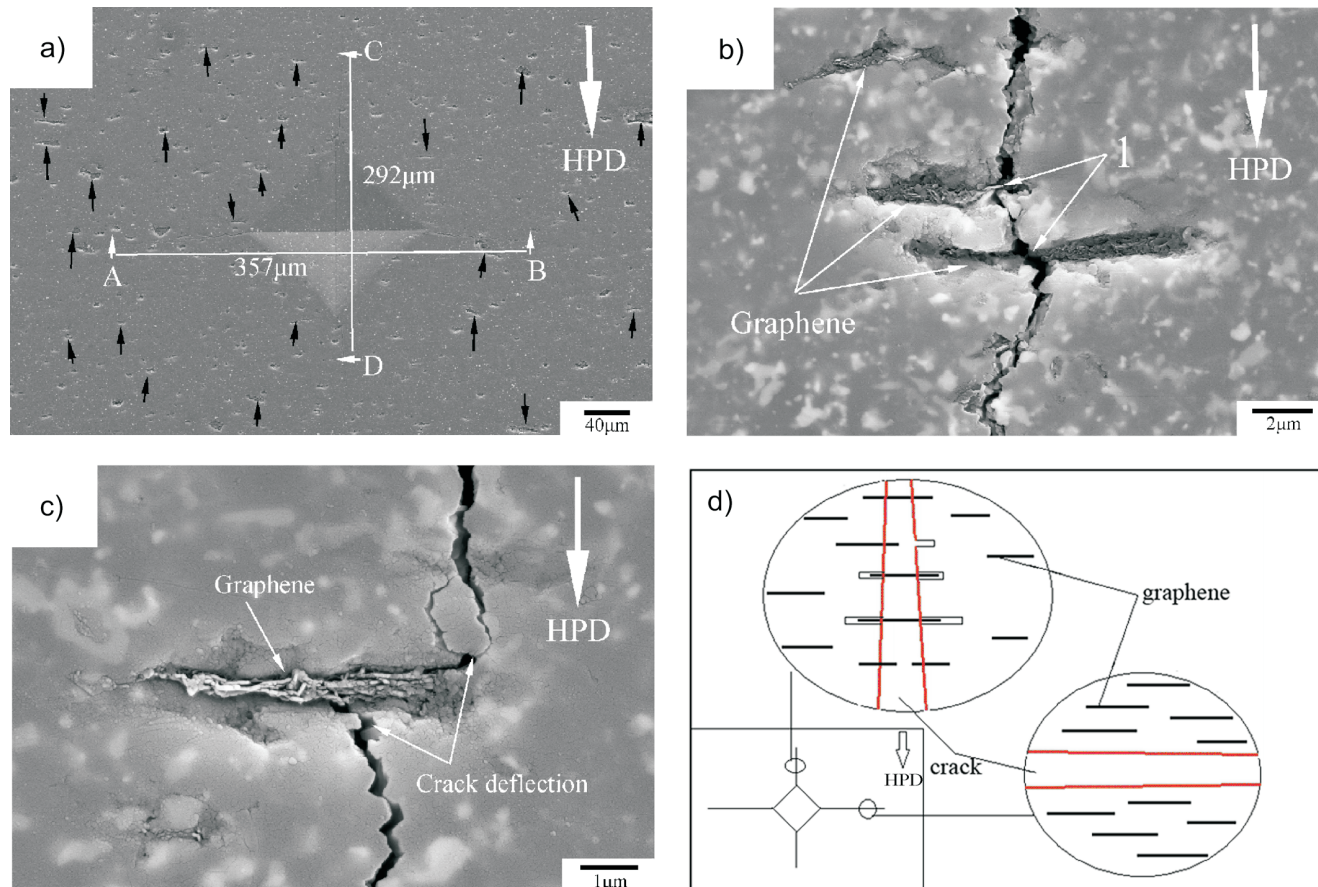


Fig. 6: SEM micrographs of STG<sub>1</sub> composite of (a) indentation morphology, (b) crack penetrates through GPLs, (c) crack deflection and (d) sketch map of crack propagation.

#### IV. Conclusions

GPLs/TiC/Si<sub>3</sub>N<sub>4</sub> composite was prepared by means of the hot pressing sintering process at 1700 °C for 60 min under 25 MPa pressure. GPLs exhibit an orientational distribution in the composite, which results in the fracture toughness of the composite in HPD being greater than that in PHPD. GPLs/TiC/Si<sub>3</sub>N<sub>4</sub> composite containing 1 wt% GPLs exhibits the highest fracture toughness of 9.6 MPa · m<sup>1/2</sup> in HPD, while its fracture toughness in PHPD is only 7.3 MPa · m<sup>1/2</sup>. The Raman spectrum shows that the I<sub>D</sub>/I<sub>G</sub> ratio in PHPD is greater than that in HPD. Crack deflection, graphene bridging and the pull-out of graphene can obviously improve the fracture toughness of composites. The developed GPLs/TiC/Si<sub>3</sub>N<sub>4</sub> composite with anisotropic fracture toughness may be used in different applications depending on the requirements, such as cutting tools, dies and other engineering parts.

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