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Laser-Induced Graphene/*h*-BN Laminated Structure to Enhance the Self-Lubricating Property of Si₃N₄ Composite Ceramic

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Abstract: Incorporating graphene as ceramic additives can significantly enhance both the toughness and self-lubricating characteristics of ceramic matrices. However, due to the difficult dispersion and easy agglomeration of graphene, the preparation process of composite ceramics still faces many problems. In this study, a laminated laser-induced reduced graphene oxide/hexagonal boron nitride (L-rGO/*h*-BN) was introduced as an additive into a silicon nitride matrix, then a silicon nitride/reduced graphene oxide/hexagonal boron nitride (Si₃N₄/L-rGO/*h*-BN) ceramic composite was successfully synthesized using Spark Plasma Sintering technology. This approach led to enhancements in both the mechanical and self-lubricating properties of silicon nitride ceramics. This is due to the good monodispersity of the incorporating graphene in the silicon nitride matrix. The flexural strength and fracture toughness of the ceramic composite experienced notable increases of 30.4% and 34.4%, respectively. Tribological experiments demonstrate a significant enhancement in the self-lubricating performance of ceramic composites upon the incorporation of L-rGO/*h*-BN. The coefficient of friction and wear spot diameter experienced reductions of 26.6% and 21%, respectively. These improvements extend the potential industrial applications of Si₃N₄/L-rGO/*h*-BN ceramic composites. Throughout the friction process, the evenly exposed rGO and *h*-BN demonstrate an effective self-lubricating effect on the wear surface. This research paves the way for a novel approach to fabricating high-performance self-lubricating structural ceramics.

Keywords: laser irradiation in liquid; graphene; hexagonal boron nitride; Si₃N₄ composite ceramic; self-lubricating



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1. Introduction

Silicon nitride (Si₃N₄), recognized as a crucial engineering structural ceramic [1–3], has garnered widespread usage due to its exceptional properties, including high strength, elevated hardness, outstanding oxidation resistance, low coefficients of friction (COF), resistance to creep, thermal shock resistance, and corrosion resistance [4–9]. Currently, Si₃N₄ finds extensive application in automotive parts [10], mechanical lubrication bearings [11] and high-performance cutting lubrication tools [2,12–15]. As science and technology progress rapidly, the demand for Si₃N₄ structural ceramics in high-end technical equipment is escalating. This includes the need for more intricate structures [16,17] and lower COF [18]. The two-dimensional graphene network structure formed by the *sp*² hybridization of single-layer carbon atoms exhibits remarkable attributes such as high strength, toughness, and excellent self-lubrication properties. Therefore, the Young's modulus and intrinsic strength can reach 1000 GPa and 130 GPa [19,20]. Graphene as an additive

can greatly improve the mechanical properties of composite materials [21,22]. The incorporation of graphene as a ceramic additive has been shown to significantly enhance the toughness and self-lubrication properties of ceramics [23–25].

However, challenges, like graphene's non-hydrophilic and non-oil-philic nature, low density, and tendency to aggregate, greatly hinder its application in ceramics [26]. Currently, there are three promising methods aimed at improving the dispersion stability of particles in the liquid phase [27,28]. The first method involves employing the steric stability mechanism, which entails introducing large long-chain molecules onto the surface of particles to impede agglomeration. The second method relies on the electrostatic stabilization mechanism, where suitable dispersants are chosen to ensure that particles carry similar charges on their surfaces, thereby enhancing dispersion. The third approach, known as the cooperative stability mechanism, involves introducing appropriate dispersants into the liquid phase, enabling a synergistic effect between steric and electrostatic stabilization mechanisms to achieve stable particle dispersion. However, these methods necessitate the use of chemical reagents, entail complex procedures, offer moderate modification effects, and can contribute to environmental pollution. Hence, there is a pressing need for a simple, environmentally friendly method for graphene surface modification.

Graphene, as an additive for ceramic-based materials, can greatly improve the mechanical properties and self-lubrication properties of ceramic materials. However, the easy agglomeration and low density of graphene limit its application in ceramic materials. In our previous research work [29], we successfully synthesized reduced graphene oxide/hexagonal boron nitride (L-rGO/h-BN) composites using laser irradiation in liquid. The h-BN and rGO exhibited a uniform distribution in sheet and sphere structures. Laser irradiation induced a loosening effect on the rGO due to the high temperature and pressure, while also increasing its surface charge, thus facilitating dispersion within the matrix. In addition, the introduction of h-BN improves the density of L-rGO/h-BN composites, addressing the challenges of poor dispersion and easy agglomeration associated with the low density of graphene within the matrix.

Therefore, we propose L-rGO/h-BN composites as additives into Si_3N_4 -based ceramics, and prepare silicon nitride/reduced graphene oxide/hexagonal boron nitride (Si_3N_4 /L-rGO/h-BN) ceramic composites by Spark Plasma Sintering (SPS) technology. Using the structural advantages of L-rGO/h-BN composite material enables the achievement of excellent dispersion within Si_3N_4 -based ceramics. As a result, this approach enhances both the mechanical and the self-lubricating properties of the ceramic materials.

2. Experimental Section

2.1. Preparation of Si_3N_4 /L-rGO/h-BN Ceramic Composites

(1) Design of raw materials and components

In this experiment, $\alpha\text{-Si}_3\text{N}_4$ was used as the main component, while the additive consisted of L-rGO/h-BN composite prepared through laser irradiation in liquid. Additionally, Al_2O_3 and Y_2O_3 were used as the composite sintering additives, with anhydrous ethanol serving as the dispersion medium, and polyethylene glycol was used as the dispersant. The key parameters of the main raw material used are illustrated in Table S1.

During the experiment, Si_3N_4 /L-rGO/h-BN ceramic composites were prepared by dual power supply spark plasma sintering system (SPS-625HF, Fuji Electric Co., Ltd., Tokyo, Japan). The matrix of Si_3N_4 /L-rGO/h-BN ceramic composite is composed of $\alpha\text{-Si}_3\text{N}_4$, Al_2O_3 , and Y_2O_3 , with a volume ratio of 90:3:7, respectively. The addition amounts of L-rGO/h-BN composites varied at 0.25 wt%, 0.5 wt%, 0.75 wt%, 1 wt%, and 1.25 wt% of the matrix mass of the above Si_3N_4 /L-rGO/h-BN ceramic composites, respectively, and the addition amount of dispersant polyethylene glycol was 2% of the matrix mass.

(2) Preparation process

The preparation process flow chart is shown in Figure 1. The specific process flow is as follows.

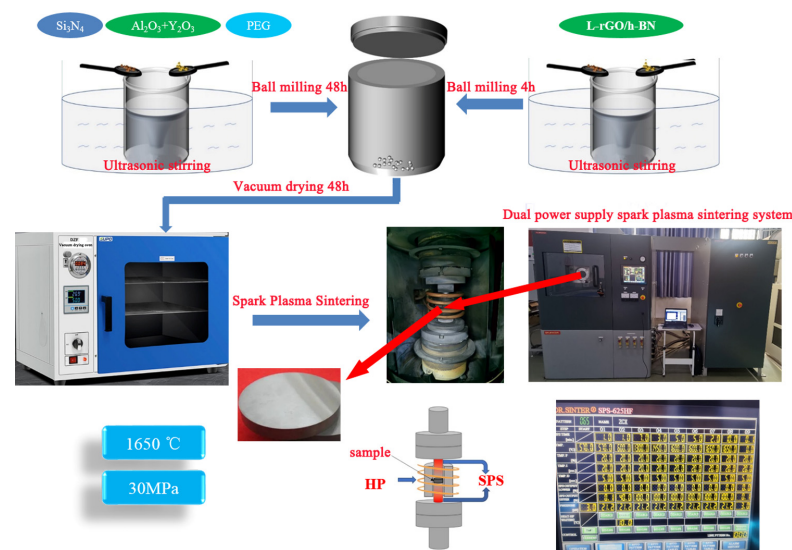


Figure 1. Flowchart of the preparation process of $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composite.

(1) Weigh 12 g $\alpha\text{-Si}_3\text{N}_4$, 0.5 g Al_2O_3 , and 1.5g Y_2O_3 and add them to the beaker, and then add 100 mL anhydrous ethanol to the beaker to make mixed solution A. (2) Weigh 0.28g polyethylene glycol and add it to 30 mL anhydrous ethanol, stir it in a water bath at 60 °C for 10 min, wait for the polyethylene glycol to be completely dissolved, and add it to mixed solution A to make mixed solution B, and then stir mixed solution B ultrasonically for 4 h. (3) Mixed solution B was added to the ball mill tank, the aluminum oxide ball was used, the mass ratio of the ball was 10:1, and the ball was ground for 44 h under nitrogen protection atmosphere. (4) Weigh 35 mg L-rGO/h-BN composite material and add it to 20 mL anhydrous ethanol, ultrasonically stirring for 1 h to make solution C. (5) After 44 h ball milling of mixed solution B, solution C was added to mixed solution B, and the mixed slurry was obtained after continued ball milling for 4 h. (6) After ball milling, dry the mixed paste in a vacuum drying oven for 48 h at a temperature of 100 °C, and pass through a 200-mesh sieve after drying. (7) The mixture is dried and sieved and added to the mold. The mold diameter is about 30 mm and the sintering thickness is 5 mm. (8) The sintering temperature was 1650 °C, the sintering pressure was 30 MPa, the heating rate and holding time are shown in Table S2, and the sintering was cooled naturally after completion. (9) The as-prepared $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composite material was cut through the inner circle slice, coarse grinding, and fine grinding by the grinder, and then ground on the ground glass. The mechanical properties of the ground material were tested and the microstructure of the cross-section of the composite was observed. (10) The sintering process of different L-rGO/h-BN addition amount is different except for step (4); the other processes are the same.

2.2. Material Characterizations

X-ray diffractometer (XRD, D8-Advance, Bruker, Billerica, MA, USA) was used to analyze the crystal phase of raw powder material of the ceramic material before sintering and after sintering, in order to analyze the crystal pattern change before and after sintering. The morphology of the materials before and after sintering and the distribution of elements on the surface of the materials after sintering were analyzed by scanning electron microscope (SEM, FEI Quanta 250 FEG, FEI Company, Hillsboro, OR, USA). The bulk sample of $10\ \mu\text{m} \times 20\ \mu\text{m} \times 100\ \text{nm}$ was prepared by using double focused ion beam electron microscope (FIB, Helios 5 CX, Thermo Fisher Scientific, Waltham, MA, USA). HAADF-STEM imaging and EDS analysis were performed by double spherical aberration correction transmission electron microscopy (HAADF-STEM, Spectra 300, Thermo Fisher Scientific).

2.3. Mechanical Property Test

The apparent density of ceramic composite materials was measured by the Archimedes water immersion method. The relative density of ceramic composite materials is then calculated. Vickers hardness was measured by the indentation method using a load of 196 N with holding time of 15 s on the polished surface. The fracture toughness was measured by the single notch beam method. The prefabricated width and depth of the middle area of the sample are about 0.2 mm and 1 mm, and the step speed of the indenting head load is $0.05 \text{ mm} \cdot \text{min}^{-1}$. The three-point bending strength test method was used to test the bending strength of the material with a loading rate of $0.5 \text{ mm} \cdot \text{min}^{-1}$ and sample span of 30 mm.

2.4. Evaluation of the Tribological Property

The tribological properties of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composites were evaluated using high-speed reciprocating friction and wear test machine (MGW-02, Jinan Yihua Tribology Testing Technology Co., Ltd., Jinan, China). The method of ball-on-disc reciprocating motion friction is adopted. The experimental equipment and parameters are shown in Figure S1. A silicon nitride ceramic ball (diameter 6 mm, Shanghai Institute of Materials Co., Ltd., Shanghai, China) was selected as the ball, and $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite material prepared in this experiment was selected as the disc. The experimental pressure is 10 N, the frequency is 5 HZ, the reciprocating distance is 7 mm, and the time is 20 min. During the experiment, the computer automatically recorded the COF data. In order to ensure the accuracy of the data, the friction experiment was repeated 3 times for each sample and the average value was taken as the COF value of the friction experiment. The COF data curve presented in this study is the average every 100 s.

After the experiment was completed, the surface of the friction pair was cleaned three times with petroleum ether, and then cleaned three times with anhydrous ethanol. The wear spot diameter (WSD) and morphology of the worn surface were observed by three-dimensional optical microscope (Contour Elite K, Bruker). The wear surface morphology and surface element distribution of different samples were observed by scanning electron microscope (SEM, FEI Quanta 250 FEG), and the self-lubricating mechanism was analyzed.

3. Results and Discussion

3.1. Phase Analysis of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ Ceramic Composites

$\alpha\text{-Si}_3\text{N}_4$ possesses high hardness and wear resistance; however, due it is equiaxed structure, its fracture toughness is relatively low. In contrast, $\beta\text{-Si}_3\text{N}_4$ exhibits a long columnar crystal structure, offering comparatively higher fracture toughness, and certain self-lubricating properties [30]. Consequently, the sintering process in this study aimed to convert $\alpha\text{-Si}_3\text{N}_4$ into $\beta\text{-Si}_3\text{N}_4$. Figure 2 illustrates the XRD pattern of the material before and after sintering. As we can clearly see, the XRD pattern of the raw material shows an obvious $\alpha\text{-Si}_3\text{N}_4$ diffraction peak before sintering [31,32], along with sintering additives Al_2O_3 and Y_2O_3 . The appearance of the $h\text{-BN}$ diffraction peak indicates the successful addition of $\text{L-rGO}/h\text{-BN}$ composites to the raw material. However, the XRD pattern does not reveal a GO diffraction peak, attributed to the poor crystallization of GO. Following sintering at a high temperature of 1650°C , the XRD pattern shows the exclusive presence of $\beta\text{-Si}_3\text{N}_4$ crystals [33], while the diffraction peaks of Al_2O_3 , Y_2O_3 , and $h\text{-BN}$ have disappeared, which is associated with low content of these substances and robust crystallinity of $\beta\text{-Si}_3\text{N}_4$. This outcome further confirms the successful transformation of $\alpha\text{-Si}_3\text{N}_4$ into $\beta\text{-Si}_3\text{N}_4$.

3.2. Mechanical Property Analysis of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ Ceramic Composites

As depicted in Figure 3a, the relative density of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite exhibits a trend of initially increasing and then decreasing with the rise in $\text{L-rGO}/h\text{-BN}$ addition. When we further increase the concentration up to 0.75 wt%, the relative density reaches 98.9%, indicating maximal densification of the material after sintering at this concentration. Figure 3b shows the Vickers hardness value of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic

composite at different addition concentrations. Notably, as the concentration of addition increases, there is a discernible decrease in Vickers hardness of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite. Even at 1.25 wt% addition concentration, the Vickers hardness of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite continues to decrease. The Vickers hardness value decreased by 14.4% from the initial 15.35 GPa to 13.14 GPa, which is the result of the addition of flexible L-rGO/ $h\text{-BN}$, but the hardness can also meet the hardness requirements within the acceptable range of most friction pairs. Figure 3c,d show the flexural strength and fracture toughness values of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite at different addition concentrations. It can be seen from Figure 3c,d that both the flexural strength and fracture toughness increase first and then decrease with the increase in L-rGO/ $h\text{-BN}$ addition concentration. At 0.75 wt%, the bending strength and fracture toughness reached the maximum values of 887 MPa and $8.6 \text{ MPa}\cdot\text{m}^{1/2}$, respectively, which increased by 30.4% and 34.4%, respectively. Indeed, these results can be attributed to the effective dispersion of L-rGO/ $h\text{-BN}$ in Si_3N_4 -based ceramics, giving full play to its excellent mechanical properties.

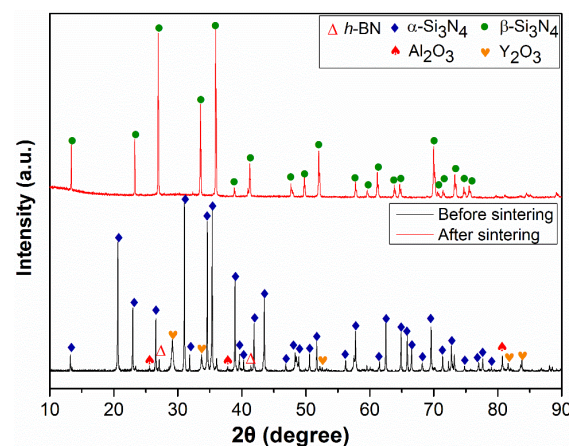


Figure 2. XRD pattern of the material before and after sintering.

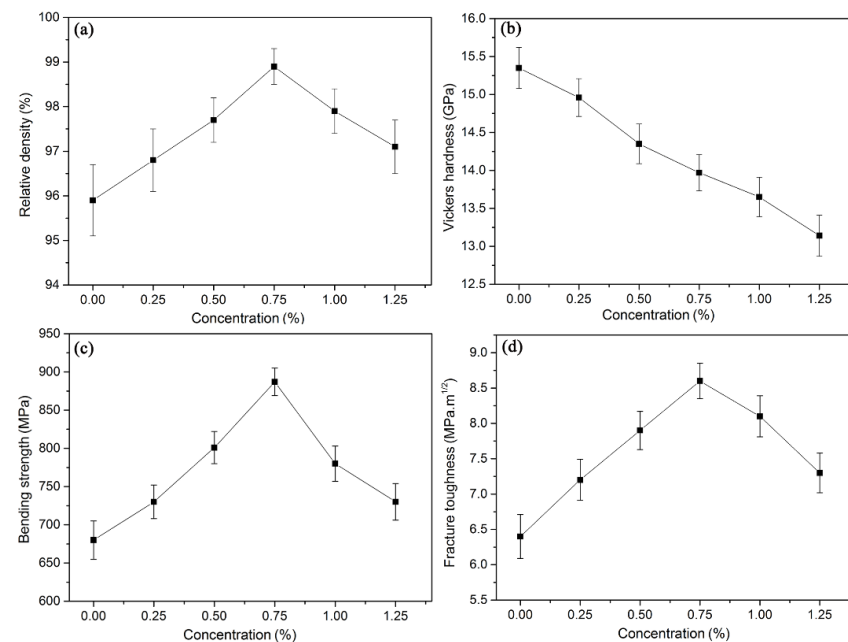


Figure 3. Relative density and mechanical properties of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composites at different L-rGO/ $h\text{-BN}$ addition concentrations: (a) relative density; (b) Vickers hardness; (c) bending strength; (d) fracture toughness.

3.3. Morphology and Elemental Analysis of $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ Ceramic Composites

Figure S2 demonstrates the image of the $\alpha\text{-Si}_3\text{N}_4$ raw material under SEM at different magnifications. As shown in Figure S2, the raw material presents an acicular crystal morphology, which is consistent with the crystal morphology of $\alpha\text{-Si}_3\text{N}_4$ [34] and consistent with the results of XRD diffraction images. The cross-section SEM images of the $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composite at different L-rGO/h-BN addition concentrations are shown in Figure 4. As can be seen from Figure 4, after SPS sintering of the $\alpha\text{-Si}_3\text{N}_4$ raw material, the grain size changes from needle to columnar, indicating that $\beta\text{-Si}_3\text{N}_4$ has been successfully sintered [35,36]. When L-rGO/h-BN is not added, the ceramic composite after sintering contains certain pores, and the sintering effect is not good, as shown in Figure 4a. With the addition of L-rGO/h-BN (0.25 wt% and 0.5 wt%), the number of pores in the ceramic composite decreases, which is because L-rGO/h-BN is stably dispersed in the matrix. During the sintering process, the interaction between matrix grains is impeded, restraining abnormal grain growth and promoting grain refinement. However, cracks (Figure 4b) and particle size inequality (Figure 4c) still exist after sintering at this concentration. When the concentration reached 0.75 wt%, the ceramic composite exhibited the highest density after sintering, and the L-rGO/h-BN additive was closely combined with the ceramic matrix. During this period, the $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composite showed the highest bending strength and fracture toughness, manifesting in optimal mechanical property index, as shown in Figures 3 and 4d. With the continuous addition of L-rGO/h-BN, due to the excessive concentration of the additive, agglomeration occurs to a certain extent and certain pores are formed, resulting in a weak area inside the ceramic composite, resulting in a decrease in mechanical properties [37,38], as shown in Figures 3 and 4e,f. From the enlarged SEM image of the cross-section of $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composite (Figure 5a,b), it can be more clearly found that L-rGO/h-BN in the ceramic composite is tightly bound to the Si_3N_4 ceramic matrix when the concentration is 0.75 wt%, while the concentration is 1.25 wt%. The graphene in the ceramic composite was agglomerated to some extent, and L-rGO/h-BN was loosely bound to the Si_3N_4 ceramic matrix, resulting in porosity, which reduced the mechanical properties of the material.

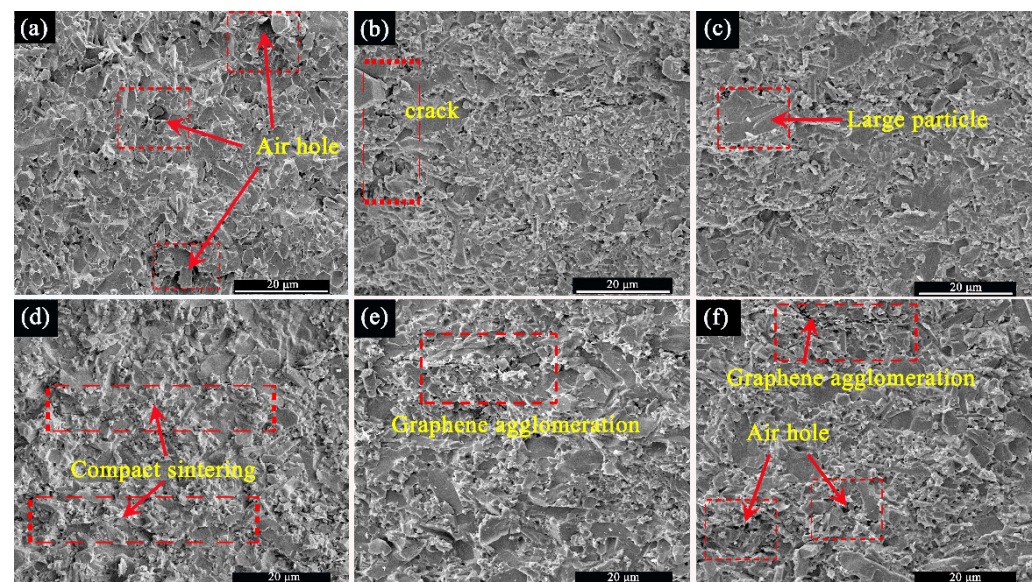


Figure 4. SEM images of cross-sections of $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composites at different L-rGO/h-BN addition concentrations: (a) 0 wt%; (b) 0.25 wt%; (c) 0.5 wt%; (d) 0.75 wt%; (e) 1 wt%; (f) 1.25 wt%.

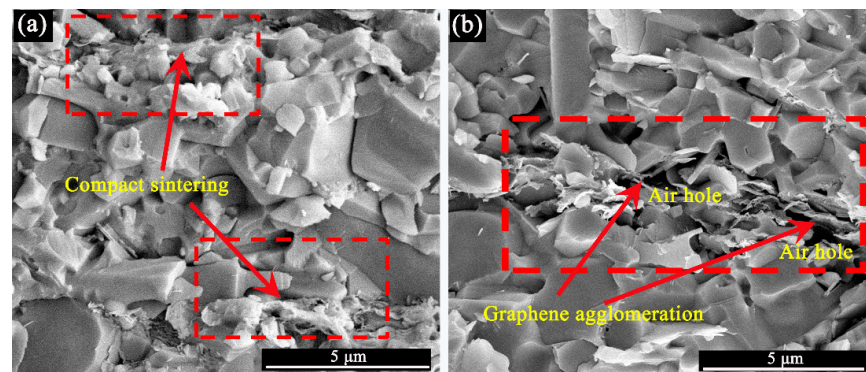


Figure 5. SEM enlarged images of $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composites at different L-rGO/h-BN addition concentrations: (a) 0.75 wt%; (b) 1.25 wt%.

In order to analyze the distribution of elements inside the $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composite after sintering, the surface element distribution analysis was carried out on the cross-section of the ceramic composite with the optimal addition amount of 0.75 wt% L-rGO/h-BN, as shown in Figure 6. Figure 6a is the SEM image of the cross-section of the ceramic composite material. EDS element analysis was carried out at the L-rGO/h-BN additive position (point 1), as shown in Figure 6b. It can be seen that there are C, B, and N elements at point 1, which confirms the successful addition of L-rGO/h-BN. At the same time, it can be seen that it contains O, Si, Al, and Y elements, which is caused by the presence of Si_3N_4 and sintering additives Al_2O_3 and Y_2O_3 in ceramic composite materials. Scanning analysis of B and C elements on the cross-section of Figure 6a shows that B and C elements are evenly distributed in $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composite, as shown in Figure 6c,d, indicating that the added L-rGO/h-BN is evenly dispersed in the ceramic composite. Thus, the excellent mechanical properties of the ceramic composite can be ensured, and the mechanical properties of $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composite can be improved.

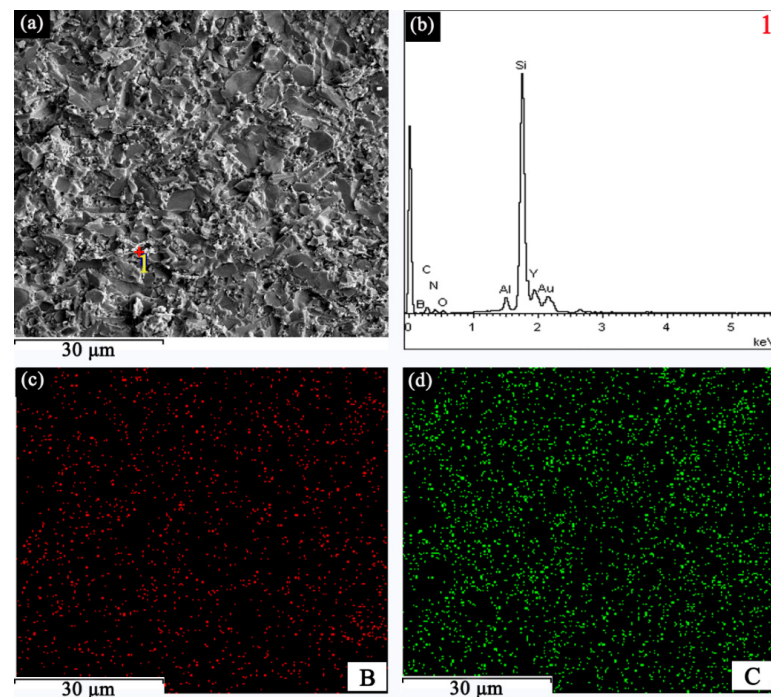


Figure 6. SEM image of $\text{Si}_3\text{N}_4/\text{L-rGO}/\text{h-BN}$ ceramic composite section and EDS analysis of elements at 0.75 wt% added concentration: (a) SEM images; (b) the EDS spectrum at point 1 in Figure (a); (c) B element mapping image of Figure (a); (d) C element mapping image of Figure (a).

In order to further analyze the bonding state of L-rGO/*h*-BN and Si₃N₄ ceramic matrix inside Si₃N₄/L-rGO/*h*-BN ceramic composite material, the sintered ceramic composite material was micro-processed using FIB, and finally thinned into a 10 μm × 20 μm × 100 nm flake sample, as shown in Figure S3. Then, the samples were subjected to HAADF-STEM imaging and EDS analysis by double-spherical aberration correction transmission electron microscopy, as shown in Figure 7. It can be seen from Figure 7a,b that after sintering, L-rGO/*h*-BN and Si₃N₄ ceramic matrix in Si₃N₄/L-rGO/*h*-BN ceramic composite is densely bonded, which leads to the improvement of the comprehensive mechanical properties of Si₃N₄/L-rGO/*h*-BN ceramic composite. The EDS mapping images of C, B, N, and Si elements (Figure 7c–f) show the distribution of elements more intuitively. The distribution of sintering additives Al₂O₃ and Y₂O₃ is shown in Figure 7g–i. It can be seen from Figure 7g–i that Al₂O₃ and Y₂O₃ are filled in the Si₃N₄ ceramic matrix and are closely combined with Si₃N₄, and the sintering effect is good.

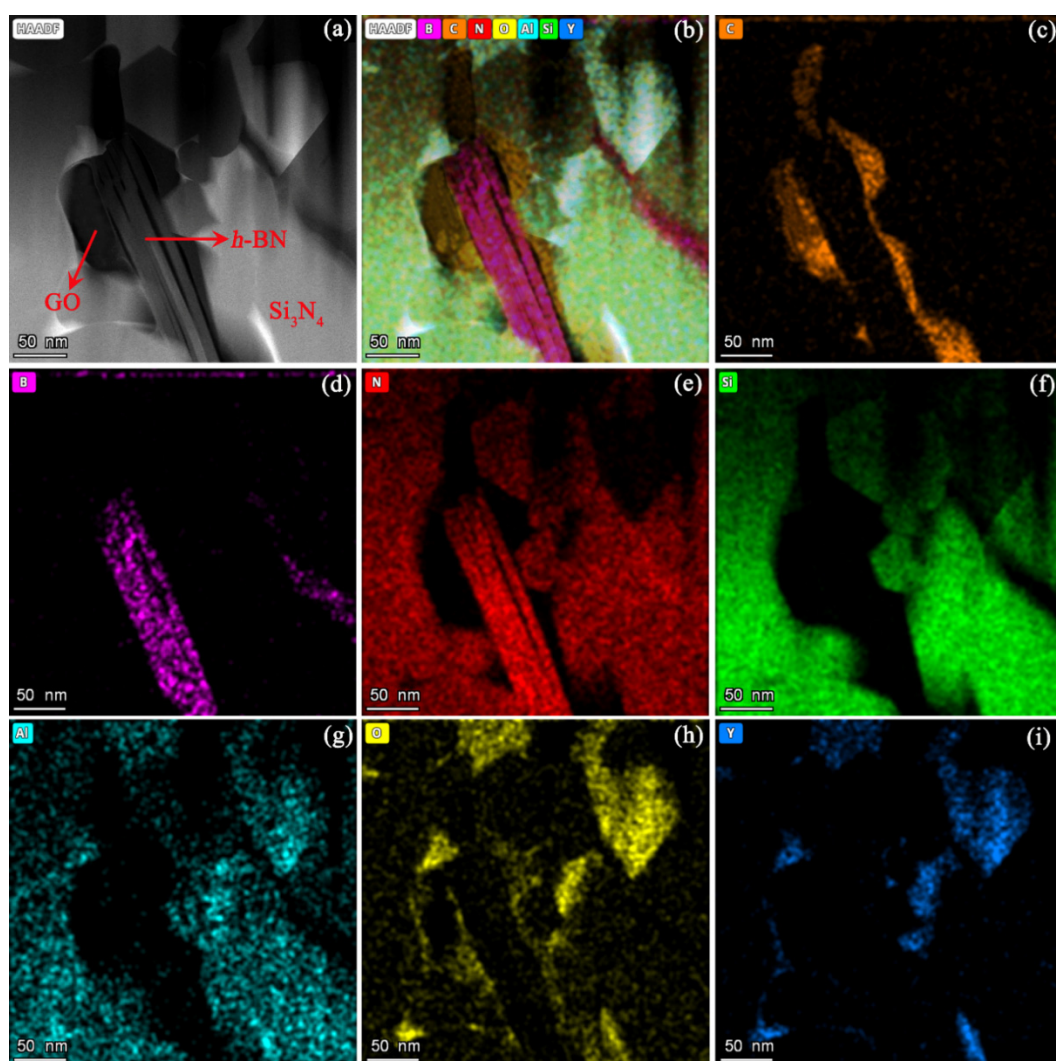


Figure 7. STEM images of Si₃N₄/L-rGO/*h*-BN ceramic composites (0.75 wt% L-rGO/*h*-BN) and corresponding EDS mapping images: (a) STEM images; (b) EDS mapping images; (c) EDS mapping image of C element; (d) EDS mapping image of B element; (e) EDS mapping image of N element; (f) EDS mapping image of Si element; (g) EDS mapping image of Al element; (h) EDS mapping image of O element; (i) EDS mapping image of Y element.

3.4. Friction Performance Analysis

The self-lubrication performance of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite was analyzed by using the reciprocating friction test method of ball-on-disc, as shown in Figure 8. Figure 8a shows the change of COF curve of ball-on-disc friction test of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composites prepared with different concentrations of L-rGO/ $h\text{-BN}$ (0 wt%, 0.25 wt%, 0.5 wt%, 0.75 wt%, 1 wt%, and 1.25 wt%) over time. As displayed in Figure 8a,b, when L-rGO/ $h\text{-BN}$ is not added, the average COF of the ball-on-disc friction experiment is the highest, at 0.537. The friction curve is unstable with large amplitude, and the standard deviation of the COF is 0.0086 (Figure S4a), while the COF tends to be stable after L-rGO/ $h\text{-BN}$ is added. With the addition of L-rGO/ $h\text{-BN}$, COF showed a trend of decreasing first and then increasing. When the addition concentration was 0.75 wt%, the average COF dropped to 0.394, with the largest decrease, reaching 26.6% (Figure 8b), showing excellent self-lubrication effect. At this time, the COF curve is smoother, and the standard deviation is reduced to 0.0048. Compared with pure Si_3N_4 , the standard deviation of the COF is reduced by 44.2% (Figure S4a). When the addition concentration was greater than 0.75 wt%, the COF began to increase, and when the addition concentration was 1.25 wt%, the average COF reached 0.512, but it was still smaller than the COF without L-rGO/ $h\text{-BN}$ friction experiment. This indicates that the self-lubricating effect of ceramic composite can be optimized only when the concentration of L-rGO/ $h\text{-BN}$ is optimal, and the optimal concentration of L-rGO/ $h\text{-BN}$ in this study is 0.75 wt%.

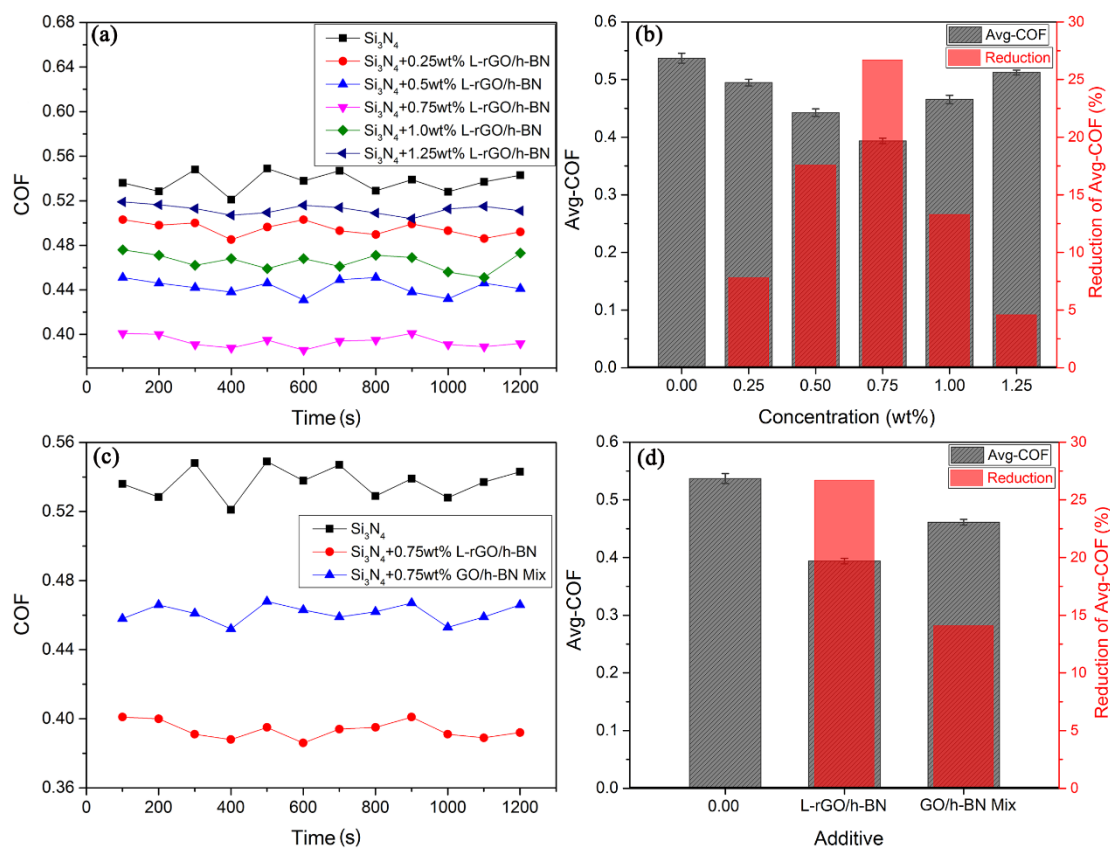


Figure 8. Ball-on-disc friction experiments of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composites prepared by adding different concentrations of L-rGO/ $h\text{-BN}$: (a) changes of COF curve; (b) the corresponding average COF and the COF reduction compared with pure Si_3N_4 disc. Ball-on-disc friction experiments of Si_3N_4 -based ceramic composites prepared by L-rGO/ $h\text{-BN}$ and GO/ $h\text{-BN}$ at 0.75 wt% concentration: (c) changes of COF curve; (d) the corresponding average COF and the COF reduction compared with pure Si_3N_4 disc.

To further demonstrate the improvement of self-lubrication performance of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite by $\text{L-rGO}/h\text{-BN}$ sheet/ball structure after treatment by laser irradiation in liquid, we added the non-laser-treated $\text{GO}/h\text{-BN}$ mechanical mixture into the Si_3N_4 ceramic matrix at an optimal concentration (0.75 wt%). After that, $\text{Si}_3\text{N}_4/\text{GO}/h\text{-BN}$ ceramic composite was prepared by the same sintering process, and $\text{Si}_3\text{N}_4/\text{GO}/h\text{-BN}$ ceramic composite was used as the friction pair to carry out the ball-on-disc friction experiment. The change curve of COF over time is shown in Figure 8c. As depicted in Figure 8c,d, after adding $\text{GO}/h\text{-BN}$ mechanical mixture, COF also decreased from 0.537 to 0.461, a decrease of 14.2%, but the decrease was smaller than that of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite. At this time, the standard deviation of the COF is 0.005, which is greater than the standard deviation of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite (Figure S4b). This is due to the special sheet/ball composite structure of $\text{L-rGO}/h\text{-BN}$, which realizes uniform and stable graphene dispersion in the Si_3N_4 ceramic matrix, thus improving the self-lubricating effect of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite. The $\text{GO}/h\text{-BN}$ mechanical mixture cannot be uniformly dispersed in Si_3N_4 -based ceramics, which limits the self-lubricating effect of graphene on Si_3N_4 -based ceramics.

Figure 9 is the average WSD and wear morphology of Si_3N_4 ball after the ball-on-disc friction experiment. As can be seen from Figure 9a,c, when $\text{L-rGO}/h\text{-BN}$ is not added, the WSD of Si_3N_4 ball is 1172 μm after the ball-on-disc friction test. With the increase in $\text{L-rGO}/h\text{-BN}$ addition concentration, the WSD of Si_3N_4 ball shows a trend of decreasing first and then increasing. The WSD decreased to 926 μm , with the largest decrease of 21% (Figure 9a,e), and the self-lubricating effect was the best at this time. When the addition concentration was greater than 0.75 wt%, the WSD began to increase, and when the addition concentration was 1.25 wt%, the WSD reached 1134 μm , which was still smaller than the WSD without $\text{L-rGO}/h\text{-BN}$ friction experiment (Figure 9a). In order to compare the influence of $\text{L-rGO}/h\text{-BN}$ sheet/ball composite structure on the self-lubrication effect of ceramic composite, $\text{Si}_3\text{N}_4/\text{GO}/h\text{-BN}$ ceramic composite prepared by adding $\text{GO}/h\text{-BN}$ mechanical mixture was used as a comparative experiment. The friction test results showed that after adding 0.75 wt% $\text{GO}/h\text{-BN}$ mixture, the WSD is 1020 μm (Figure 9b,d), the reduction is 13%, and the self-lubrication effect is lower than that of $\text{L-rGO}/h\text{-BN}$. By comparing Figure 9c–e, it can be found that when $\text{L-rGO}/h\text{-BN}$ composite material is not added, the WSD is not only the largest, but there is also the deepest wear furrow on the surface, indicating serious wear. After adding $\text{GO}/h\text{-BN}$ mechanical mixture and $\text{L-rGO}/h\text{-BN}$, the WSD became smaller, and the surface wear marks began to become shallow. Among them, the appearance of the wear spots changed most significantly after adding $\text{L-rGO}/h\text{-BN}$. After adding $\text{L-rGO}/h\text{-BN}$ friction experiment, Raman analysis was performed on the wear surface, and the results are shown in Figure S5. As can be seen from Figure S5, after the friction test, the same substance as $\text{L-rGO}/h\text{-BN}$ additive was found on the surface of the Si_3N_4 ball, indicating that the additive repaired the surface of the Si_3N_4 ball, thereby reducing wear. This fully demonstrates the significant improvement effect of $\text{L-rGO}/h\text{-BN}$ on the self-lubricating properties of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composites.

3.5. Self-Lubrication Mechanism Analysis

Figure 10 shows the SEM image of the wear marks on the surface of Si_3N_4 -based ceramic discs after the ball-on-disc friction experiment and the distribution of C element on the surface of the wear marks. It can be clearly seen from Figure 10a–c that without adding $\text{L-rGO}/h\text{-BN}$, after the friction test, the surface of the ceramic disk was seriously worn, with the widest abrasion mark reaching 1150 μm , and serious spalling occurred in some areas, as shown in the area within the rectangular box in Figure 10c. After the $\text{GO}/h\text{-BN}$ mechanical mixture was added, the surface wear degree was reduced, the width of the wear mark was reduced to 980 μm , no spalling occurred in the surface wear area, and the formation of similar lubricating film could be seen in some areas of the wear mark surface (Figure 10f). The self-lubrication performance of $\text{Si}_3\text{N}_4/\text{GO}/h\text{-BN}$ ceramic composite was improved by the addition of $\text{GO}/h\text{-BN}$ mechanical mixture, as shown in Figure 10d–f. Figure 10g–i

show the SEM image of the wear surface of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite after L-rGO/ $h\text{-BN}$ is added. At this time, the wear width is $850\text{ }\mu\text{m}$, and the wear width is reduced by 26.1% compared with pure Si_3N_4 ceramic, and the self-lubricating effect is significantly improved. More similar film formation can be found in the surface area of the abrasion (Figure 10i). In order to analyze the composition of the lubrication film on the wear surface, EDS element analysis was performed on the wear surface, as shown in Figure 10j,k. Figure 10j is the mapping image of C element in the SEM image region of Figure 10d. It can be seen from Figure 10j that C element is distributed in some areas of the surface of the wear marks, and a layer of graphene self-lubricating film is formed in some areas of the surface, which realizes a certain degree of self-lubricating of $\text{Si}_3\text{N}_4/\text{GO}/h\text{-BN}$ ceramic composite material. Figure 10k is the mapping image of C element in the SEM image region of Figure 10g. Compared with Figure 10j, it can be clearly found that C element is evenly distributed in all areas of the worn surface, and a relatively comprehensive repair of the friction area is carried out. This is also why the addition of L-rGO/ $h\text{-BN}$ is more self-lubricating than the addition of GO/ $h\text{-BN}$ mechanical mixture.

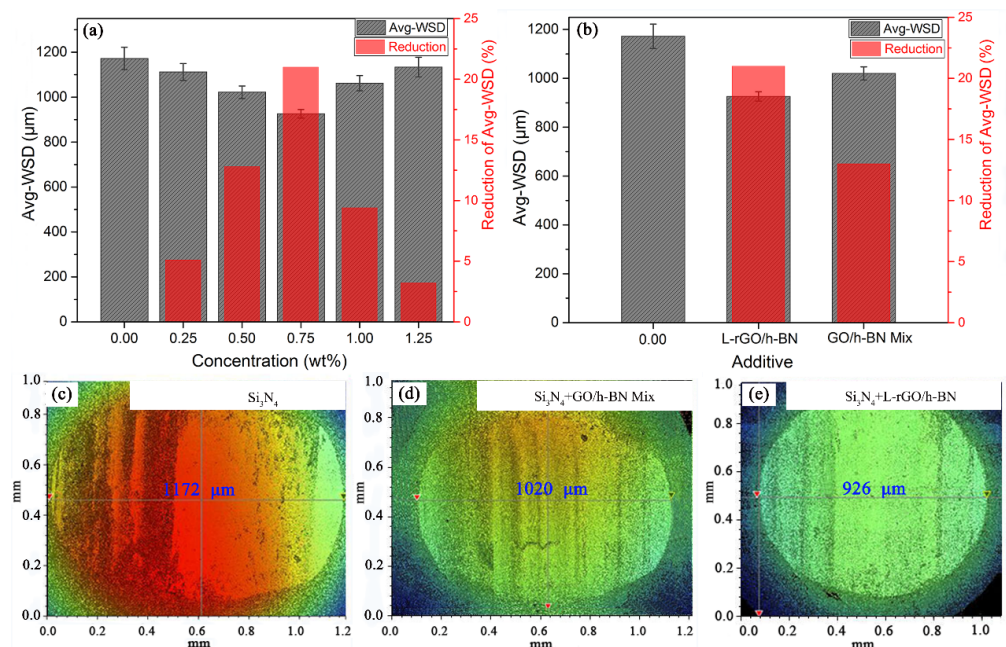


Figure 9. Average WSD and the corresponding WSD reduction compared with the pure Si_3N_4 disc of Si_3N_4 ball after friction experiment: (a) $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite prepared by adding different concentrations of L-rGO/ $h\text{-BN}$; (b) ceramic composites prepared with L-rGO/ $h\text{-BN}$ and GO/ $h\text{-BN}$ at 0.75% wt% concentration. Wear morphology of Si_3N_4 ball after friction experiment: (c) L-rGO/ $h\text{-BN}$ was not added; (d) 0.75 wt% GO/ $h\text{-BN}$ mechanical mixture was added; (e) 0.75 wt% L-rGO/ $h\text{-BN}$ was added.

Figure 11 shows the formation mechanism of self-lubricating film of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite. Figure 11a is the schematic diagram of the reciprocating friction experiment of ball-on-disc. Before the friction experiment, the surface of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite material was intact and smooth, as shown in Figure 11a. L-rGO/ $h\text{-BN}$ is uniformly distributed in the matrix of $\text{Si}_3\text{N}_4/\text{L-rGO}/h\text{-BN}$ ceramic composite. After the friction experiment began, the Si_3N_4 ball carried out reciprocating friction movement on the surface of the ceramic composite material, and the movement trajectory is shown in Figure 11c. With the progress of friction, the surface of the ceramic composite material is worn and peeled off, as shown in Figure 11b. At this time, the uniform distribution of L-rGO/ $h\text{-BN}$ is exposed, deposited on the surface, and accumulated on the surface of the abrasion to form a self-lubricating film. On the other hand, through the previous analysis, it has been confirmed that the internal Si_3N_4 ceramic matrix and L-rGO/ $h\text{-BN}$ are

compact, coupled with the excellent mechanical properties of L-rGO/*h*-BN itself, so with the progress of friction, the additive L-rGO/*h*-BN will not be easily pulled out and broken. As a result, the self-lubricating film formed by L-rGO/*h*-BN additive on the surface of the wear marks becomes thicker and thicker, and eventually covers the surface of the wear marks, as shown in Figure 11d, thereby improving the self-lubrication performance of the Si_3N_4 /L-rGO/*h*-BN ceramic composite.

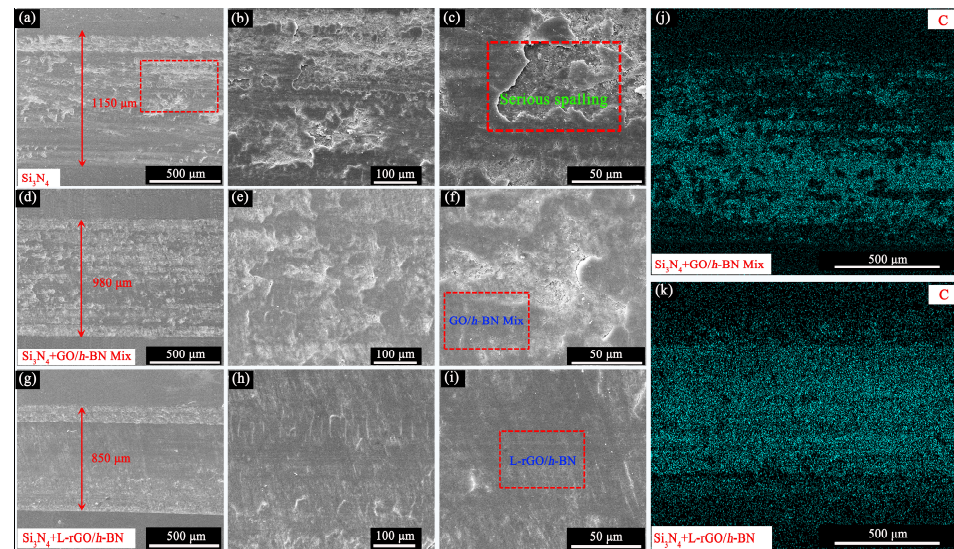


Figure 10. SEM image of surface wear marks of Si_3N_4 -based ceramic composites after friction test: (a–c) L-rGO/*h*-BN was not added; (d–f) 0.75 wt% GO/*h*-BN mechanical mixture was added; (g–i) 0.75 wt% L-rGO/*h*-BN pellet composite material was added. C element mapping image of surface wear of Si_3N_4 -based ceramic composite: (j) 0.75 wt% GO/*h*-BN mechanical mixture was added; (k) 0.75 wt% L-rGO/*h*-BN composite material was added.

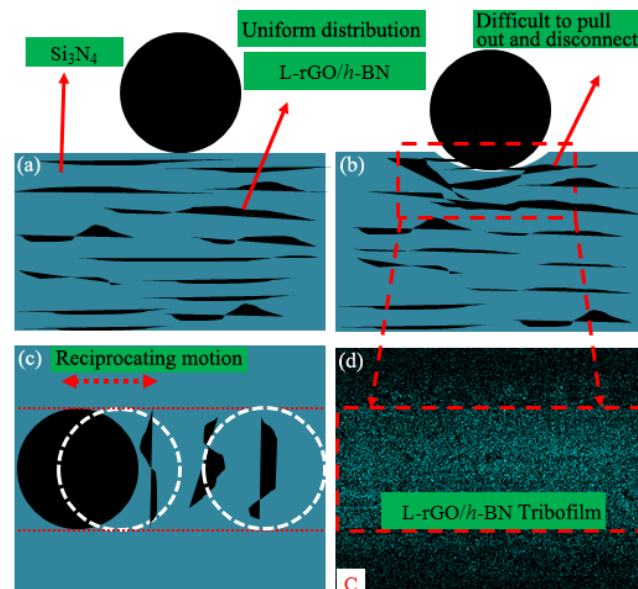


Figure 11. Formation mechanism of Si_3N_4 /L-rGO/*h*-BN ceramic composite self-lubricating film: (a) cross-section diagram of the ball-on-disc reciprocating friction experiment; (b) schematic diagram of cross-section wear in ball-on-disc reciprocating friction experiment; (c) top view of self-lubricating film formation mechanism after ball-on-disc reciprocating friction experiment; (d) the distribution of C element in the wear zone on the surface of Si_3N_4 /L-rGO/*h*-BN ceramic composite after the ball-on-disc friction experiment.

4. Conclusions

In this study, the additive for Si_3N_4 -based ceramics consisted of a composite structure of L-rGO/*h*-BN sheet/balls, which was prepared through laser irradiation in liquid. Subsequently, the Si_3N_4 /L-rGO/*h*-BN ceramic composite was successfully prepared by SPS sintering process. This method improves the mechanical properties and self-lubricating properties of Si_3N_4 -based ceramics, and improves the industrial application range of Si_3N_4 -based ceramic composites. The main conclusions are as follows:

- (1) The optimum preparation parameters of Si_3N_4 /L-rGO/*h*-BN ceramic composites are as follows. The volume ratio of α - Si_3N_4 , Al_2O_3 , and Y_2O_3 is 90:3:7, the sintering temperature is 1650 °C, the sintering pressure is 30 MPa, and the optimum concentration of L-rGO/*h*-BN additive is 0.75 wt%.
- (2) The Si_3N_4 /L-rGO/*h*-BN ceramic composite was characterized by X-ray diffractometer, scanning electron microscope, and double spherical aberration correction transmission electron microscope. After sintering, α - Si_3N_4 is successfully converted to β - Si_3N_4 . L-rGO/*h*-BN achieves good monodispersion in Si_3N_4 matrix due to its special sheet/ball composite structure. When the concentration of L-rGO/*h*-BN reaches 0.75 wt%, the Si_3N_4 /L-rGO/*h*-BN ceramic composite is highly dense after sintering, and L-rGO/*h*-BN is closely bonded with the Si_3N_4 ceramic matrix.
- (3) After the addition of L-rGO/*h*-BN, the mechanical properties of Si_3N_4 /L-rGO/*h*-BN ceramic composites are greatly improved. When the added concentration is 0.75 wt%, the relative density reaches 98.9%, and the bending strength and fracture toughness reach the maximum values, which are 887 MPa and $8.6 \text{ MPa} \cdot \text{m}^{1/2}$, respectively, with increases of 30.4% and 34.4%.
- (4) The self-lubrication performance of Si_3N_4 /L-rGO/*h*-BN ceramic composite was analyzed by ball-on-disc reciprocating friction experiment. The friction experiment shows that when the concentration of L-rGO/*h*-BN is 0.75 wt%, the COF decreases by 26.6% from 0.537 to 0.394, and the WSD decreases by 21% from 1172 μm to 926 μm . The standard deviation of COF decreases by 44.2% from 0.0086 to 0.0048, and the friction state is more stable. This is because of the special sheet/ball structure of L-rGO/*h*-BN additive and the successful sintering preparation of SPS. L-rGO/*h*-BN additive achieves effective dispersion in Si_3N_4 /L-rGO/*h*-BN ceramic composite. During the friction process, graphene is exposed and deposited on the surface of the friction pair, which not only protects the surface of the friction pair, but also shows a good self-lubricating effect.

The tribological property research method in this study is mainly the linear friction method of point-surface friction at normal temperature, and the extreme temperature, surface-surface, and rotating friction methods are not studied. In the future, the research scope should be expanded, and the self-lubricating performance of ceramic composite materials should be further improved to continuously reduce energy consumption.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/lubricants12060219/s1>, Table S1: The main raw materials and main parameters of Si_3N_4 /L-rGO/*h*-BN ceramic composite. Table S2: List of heating rate and holding time in sintering process. Figure S1: Experimental equipment and parameters of ball-disc reciprocating friction: (a) experimental equipment and (b) Experimental parameters. Figure S2: SEM image of α - Si_3N_4 raw material: (a) low power and (b) High magnification. Figure S3: FIB thinning process of Si_3N_4 /L-rGO/*h*-BN ceramic composite at 0.75 wt% added concentration: (a) Si_3N_4 /L-rGO/*h*-BN cross-section STEM images and (b) flaky sample after FIB thinning. Figure S4: Standard deviation of COF: (a) Different addition concentrations and (b) Different additives at 0.75 wt%. Figure S5: Raman spectra of wear surface on Si_3N_4 ball: (a) Wear morphology of Si_3N_4 ball after friction experiment with 0.75 wt% L-rGO/*h*-BN and (b) Raman spectra of Points 1, 2 in Figure S5 (a) and L-rGO/*h*-BN.

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