Laminated Si₃N₄-Mo Composites Produced by Hot Pressing

Wei Chen¹, Ziqiang Zhao¹, Zhaoxun Wang¹, Wenhui Hao¹

¹College of Mechanical and Electrical Engineering, Shaanxi University of Science & Technology, Xi’an 710021, P.R. China

Abstract
In this paper, the physical, mechanical and friction behavior of Si₃N₄-Mo laminated composites were investigated. It can be found that the multilayer structure could improve the fracture toughness of laminated composite compared with pure Si₃N₄. Through the thermodynamic and kinetic calculations of chemical reactions, we conclude that the main product of the interface is Mo₅Si₃ which caused poor physical and mechanical properties of Si₃N₄-Mo layered ceramics. The higher content of Mo was beneficial to hinder the diffusion of cracks and improved the fracture toughness of the material, but with the lower content of Mo, Si₃N₄-Mo laminated ceramic composite had better tribology property. In addition, with the increase of the load, the tribology property of Si₃N₄-Mo laminated ceramic composite decreased, and the friction mechanism of Si₃N₄-Mo/TC4 is a mixed wear of adhesive wear and abrasive wear.

Keywords: Ceramic composite; Multilayer structure; physical and mechanical characteristics; tribology.

1. Introduction
As one of the most important structural materials, silicon nitride (Si₃N₄) based ceramic composites had been widely used in bearings, piston pumps, engine parts and high-speed cutting tools. However, this kind of composites showed low fracture toughness in application¹,². Therefore, a method to effectively toughen Si₃N₄ based composites was greatly needed.

In the 1970s, researchers designed and prepared bionic structural ceramics by
analysing and imitating the structure of nacre shell in nature, which provided a new idea for the toughening and strengthening of ceramic materials\textsuperscript{[3, 4]}. From then on, scholars tried to add solid lubricant like BN to ceramic materials as a sandwich. D Kovar\textsuperscript{[5]} et al. prepared and studied the effect of the toughness of the weak interface layer on the mechanical properties of the Si$_3$N$_4$/BN laminated composite. The result showed that the composition of interface layer had little influence on the strength of layered materials, but the fracture work of materials decreased sharply with the increase of Si$_3$N$_4$ content. Similarly, Q Zan\textsuperscript{[6]} et al studied the Si$_3$N$_4$/BN laminated composite and found that the strength of layered materials decreased with the increase of the number of layers. Tan Jun\textsuperscript{[7]} prepared and studied B$_4$C/BN laminated ceramic composite by water-based tape casting and laminated hot-pressed sintering. It is found that the thickness ratio and the composition of the weak interfacial layer had an effect on the mechanical properties and microstructure of the layered ceramics. In the laminated ceramic composites, not only the dispersion toughening caused by adding second phase, but also the toughening mechanism such as crack deflection, bifurcation and delamination caused by the layered structure, which effectively improves the mechanical properties of the ceramic materials. In addition, many scholars added metal materials as interlayers to ceramic materials. K Zuo\textsuperscript{[8]} et al. found that the strength and toughness Al$_2$O$_3$-Ni/Ni laminated composite material was higher than that of Al$_2$O$_3$/Ni layered composite with the same structural parameters. However, the mechanical properties of layered ceramic materials have always been the focus of attention, while the tribological properties and lubrication mechanism are rarely reported.

Our group has been devoted to the tribological research of Si$_3$N$_4$ ceramic composites in various fields, and the developed Si$_3$N$_4$-hBN ceramic composites have certain practical functions in many fields\textsuperscript{[9-17]}. However, in Si$_3$N$_4$-hBN ceramic composites, the binding capacity of hBN and ceramic matrix is poor, and excessive addition of hBN will cause the ceramic composites to lose their original high strength and high hardness. According to existing research findings\textsuperscript{[11]}, the layered ceramic materials made by adding metal Mo as weak surface layer have good corrosion
resistance and can achieve toughening effect of ceramic materials. Based on this, we add Mo interface layer to Si₃N₄ ceramic composites to prepare Si₃N₄/Mo layered composites, and explore its physical and mechanical properties. We hope that this study would provide data supporting for the application of ceramic materials and polymer materials in marine engineering equipment.

2. Experimental procedure

2.1 Raw materials

In this study, commercial α-silicon nitride (Si₃N₄: 99.9% pure with an average particle size of 1.5 μm from HeFei Aijia New Material Co., Ltd.) and molybdenum (Mo: 99.0% pure from Sinopharm Chemical Reagent Co., Ltd, China) were used. Ytterbium oxide (Y₂O₃: an average particle size of 0.37 μm and purity of 99%) and aluminium oxide (Al₂O₃: an average particle size of 1.17 μm and purity of 99%) were used as sintering aids.

2.2 Fabrication procedure

The Si₃N₄ powder with 4% Y₂O₃ and 6% Al₂O₃ powders was ball-milled using zirconia oxide balls for 5 h at 100 rpm in alcohol, after that, these mixed powders were constantly stirred and dried in a drying oven. Then, the dried powders of mixed-ceramics and Mo were weighted into some shares, the compositions of ceramics and Mo powders were shown in Table 1. The ceramics and Mo powders were stacked the layers in sequence in a stainless-steel die, and the green body of multilayer sample was pressed at a pressure of 30 MPa for 10 minutes. Next, the multilayer green bodies of 11Si₃N₄-Mo and 9Si₃N₄-Mo were hot-pressed at a pressure of 30 MPa and at 1800 °C for 30 minutes in a nitrogen atmosphere, respectively. The fabrication procedure of the laminated samples is shown in Fig. 1. In addition, the pure Si₃N₄ was prepared as the contrastive sample by the same process of ball milling, drying and hot-pressing.

| Properties                  | 11Si₃N₄-Mo | 9Si₃N₄-Mo |
|-----------------------------|------------|-----------|
| Thickness ratio (of Si₃N₄ to Mo) | 11: 1      | 9: 1      |
2.3 Characterization

In this work, the specimens for tests were prepared by cutting into bars with dimensions of 25 mm × 5 mm × 5 mm for physical and mechanical properties and 25 mm × 5 mm × 5 mm for tribological properties. Hardness was determined by Vickers indentation under a load of 10 N with a dwell time of 15 s. In order to determine the indentation toughness, at least 5 Vickers indentations per specimen were made on the basis of Vickers hardness measurements. The bending strength of laminated ceramics was determined by three-point bending tests using a material test system (1036PC) with a span length of 16 mm and a crosshead speed of 0.5 mm/min. The indentation toughness was calculated from the lengths of radial cracks and indents diagonals using a formula given as follows\[^{[19]}\]:

\[
K_{IC} = 0.203 \times (\frac{c}{a})^{-3/2} \cdot \sqrt{a} \cdot HV
\]  

where, \(a\) is the half length of indentation diagonal, \(c\) is the radial half-crack length and \(HV\) is Vickers hardness of materials.

Sintered specimens were ground, polished to a range of 0.8~1 μm by a diamond grinding tool and chemically etched in molten NaOH at 400°C for 2 min. The microstructures were then studied by using a VEGA II XMU scanning electron microscope.
The tribological test of the laminated samples was conducted using a pin-on-disc tribometer against an Φ 44 mm × 6 mm TC4 disc. Before the wear test, the sintered composites were carefully polished to obtain a surface roughness of 0.1-0.3 μm. And then, the polished specimens were ultrasonically cleaned in acetone. The wear test was performed at a load of 10 and 30 N, line speed of 0.87 m/s and test duration of 20 minutes. The lubrication environment was artificial seawater prepared according to Standard ASTM D 1141-98 (as shown in Table 2). The worn surface of the composites was analyzed by scanning electron microscopy (SEM, FEI Company, Hillsboro, USA). Structure analysis of the laminated ceramics was conducted by X-ray diffraction (XRD, D/max2200PC, Rigaku, Japan).

Table 2 Chemical composition of artificial seawater

| Constituent | NaCl | Na₂SO₄ | MgCl₂ | CaCl₂ | SrCl₂ | KCl | NaHCO₃ | KBr | H₃BO₃ | NaF |
|-------------|------|--------|-------|-------|-------|-----|--------|-----|-------|-----|
| Concentration C/(g•l) | 24.53 | 4.09   | 5.20  | 1.16  | 0.025 | 0.695 | 0.201  | 0.101 | 0.027 | 0.003 |

3. Results and discussion

3.1 Phase composition

The XRD analysis of the prepared Si₃N₄/Mo layered ceramic composite material is shown in Fig. 2. The results show that the Si₃N₄ has also completed the transformation from α phase to β phase under this process, and no α-Si₃N₄ has been detected. As shown in Fig. 3, Si₃N₄ completely exist in the β phase in the form of rods. However, Mo₅Si₃ phase that is the product of the reaction between Si₃N₄ and Mo has been detected, and there is a molybdenum-silicon compound at the interface between the ceramic and the metal. The main phase formed is Mo₅Si₃. This substance has a large difference in lattice constant (a/c≈2), the coefficient of thermal expansion is anisotropy (α_c/α_a≈2), therefore, Mo₅Si₃ will have cracks during the growth of single crystals, which is also the reason for the large number of cracks found in the metal region in Figure 4. In addition, no Mo element was detected in the metal layer, indicating that Mo may remain small or have completely reacted.
Fig. 2 The XRD result of Si₃N₄/Mo laminated ceramic composites

Fig. 3 The corrosion morphology of ceramic layer of Si₃N₄/Mo laminated ceramic composites

Fig. 4 The fracture morphology of Si₃N₄/Mo laminated ceramic composites(SEM):(a) metal layer of 9Si₃N₄-Mo laminated ceramics;(b) metal layer of 11Si₃N₄-Mo laminated ceramics

3.2 Interface composition

In the overall system of layered materials, the interface layer is the key to determine the toughness of the laminated ceramic composites. Under the external
force of the material, the interface layer can effectively hinder the crack propagation through the effects of passivation, deflection, bridging, etc. Therefore, the material composition of the interface layer directly affects the performance of the material.

It can be found from Fig. 2 that Mo$_5$Si$_3$ is the main existing form of the metal region, not the original elemental Mo. In order to further explore the material composition of the interface layer and the metal layer, the EDS spectrum was linearly detected at the fracture of the Si$_3$N$_4$/Mo layered composite material. The main areas of the detection were divided into two places: one is the boundary between the Si3N4 ceramic and the metal layer, the other is near the center of the metal layer, and the detection is performed along the trajectories of "A" to "B" and "C" to "D", as shown in Fig. 5(a) and (c), the EDS line scan. The detection results are shown in Fig. 5(b) and (d).

As shown in Fig. 5(d), there is indeed elemental Mo in the area near the center of the metal layer, and when the detection gradually extends from "D" to "C", the Si element suddenly appears, passing through the "Y" area, the relative ratio with Mo element reached a stable state of about 3:5, and substances in this area was Mo$_5$Si$_3$. Therefore, when extending outward from the area near the center of the metal, the substance gradually changed from elemental Mo to Mo$_5$Si$_3$ through the transition area "Y". As shown in Fig. 5(b), the dark ceramic area is completely in the form of Si$_3$N$_4$. When the detection gradually extends from the "A" through the dark and light color boundary line (that is, the interface layer of the layered material), the element Si gradually decreases, while the Mo element began to appear and gradually increased. After the transition of the "X" region, the relative ratio of Mo and Si elements reached a stable state of about 5:3, and substances in this area was Mo$_5$Si$_3$. Therefore, when the dark ceramic area extends toward the metal layer, the substance gradually changes from Si$_3$N$_4$ to Mo$_5$Si$_3$ through the transition area "X".
Fig. 5 Fracture morphology and corresponding EDS line scan results of fracture surface of Si$_3$N$_4$/Mo laminated ceramic composite: (a) The area of layer interface; (b) the corresponding EDS line scan results of the area layer interface; (c) the area near the center of the metal layer; (d) the corresponding EDS line scan results of the area near the center of the metal layer.

According to the EDS spectrum analysis of the fracture of the layered composite material, at the layer interface of the Si$_3$N$_4$/Mo laminated ceramic composite, during the high-temperature sintering process, Si$_3$N$_4$ and Mo reacted chemically, and the Si element cracked from Si$_3$N$_4$ to combine with the Mo phase, a molybdenum-silicon compound dominated by Mo$_5$Si$_3$ was formed. According to some studies [13, 18-20], Si$_3$N$_4$ and Mo will undergo the following series of reactions at high temperature:

$$3Mo + 2Si_3N_4 \rightarrow 3MoSi_2 + 4N_2 \quad (1)$$

$$20MoSi_2 + 48Mo \rightarrow Mo_5Si + 13Mo_3Si_3 \quad (2)$$
Therefore, it can be speculated that the substance present in the transition region "X" is mainly MoSi$_2$, and the substance present in the transition region "X" is mainly Mo$_3$Si. In summary, the material distribution from the interface of the Si$_3$N$_4$/Mo laminated ceramic composite layer to the center of the metal layer is Si$_3$N$_4$→MoSi$_2$→Mo$_5$Si$_3$→Mo$_3$Si→Mo.

3.3 Mechanical properties

It can be seen from Table 3 that all three materials maintain high hardness, which is due to the phase transformation strengthening of Si$_3$N$_4$ through the high-temperature sintering process, but the appearance of Mo$_5$Si$_3$ leads to lower density and bending strength of Si$_3$N$_4$/Mo laminated ceramic composites, and the realization of the layered structure promotes the improvement of the material's fracture toughness. The thermal expansion coefficients of the two substances are different. During the cooling process of the molding, the material with the large thermal expansion coefficient shrinks greatly, correspondingly, the material with the small thermal expansion coefficient shrinks small, which produces the tensile and compressive stress at the interface between the silicon nitride composite ceramic and the metal. When the crack extends in the layer structure, the existence of residual stress causes the crack to deflect at the layer interface, thereby consuming the energy of fracture and increasing the fracture toughness of the layered material. Furthermore, the fracture toughness of 9Si$_3$N$_4$-Mo is 0.5 MPa·m$^{1/2}$ more than that of 11Si$_3$N$_4$-Mo laminated ceramic composites. Combined with Fig. 6, cracks in 9Si$_3$N$_4$-Mo mostly appear crack deflection when passing through the metal layer. While in 11Si$_3$N$_4$-Mo I laminated ceramic composites, some cracks directly penetrated the metal layer and the ceramic layer, which shows that when the content of Mo in the layer structure is high, it is beneficial to hinder the diffusion of cracks and improve the fracture toughness of the material.

| Properties | Si$_3$N$_4$ | 11Si$_3$N$_4$-Mo | 9Si$_3$N$_4$-Mo |
|------------|------------|-----------------|----------------|

Table 3 The mechanical properties of pin samples
| Porosity (%) | 0.24 | 14.20 | 20.10 |
|-------------|------|-------|-------|
| Vicker’s hardness (GPa) | 14.9 | 14.0 | 14.6 |
| Bending strength (MPa) | 818 | 275 | 330 |
| Fracture toughness (MPa·m$^{1/2}$) | 8.50 | 10.7 | 11.2 |

Fig. 6 The fracture trend of Si$_3$N$_4$/Mo laminated ceramic composites (SEM) : (a) 9Si$_3$N$_4$-Mo; (b) 11Si$_3$N$_4$-Mo

3.4 Thermodynamic analysis of interface layer

As can be seen from the analysis before the text, the Si$_3$N$_4$/Mo laminated composites have chemical reactions between composite ceramic materials and metals during high temperature sintering, and the forming compounds, such as MoSi$_2$, Mo$_5$Si$_3$ and Mo$_3$Si, extended into the central area at the layer interface. Due to the appearance of molybdenum silicides, resulting in the decrease in the bending strength and density of laminated composites. However, it’s not clear about the formation of the material at the interface of the Si$_3$N$_4$/Mo layered composite layer and the conditions under which it occurs. Therefore, we analyzes the evolutionary mechanism of material formation at the interface of the layer according to the principle of material thermodynamics.

As can be seen from the above, at high temperatures, Si$_3$N$_4$ ceramics react with Mo to form molybdenum silicides. As can be seen from the laws of thermodynamics, at high temperatures, the necessary condition for a chemical reaction to be spontaneous is that gibbs free energy was negative, therefore, we can judge whether these reactions can proceed spontaneously at the molding temperature according to this prerequisite. A mathematical expression known for gibbs free energy at a specific temperature $T$:

$$\Delta G^0_T = \Delta H^0_{298} - T \Delta S^0_{298} + \int_{298}^T C_p \, dT - T \int_{298}^T \left( \frac{C_p}{T} \right) dT$$

(4)

Among them: $\Delta G$ is the difference in Gibbs free energy of the chemical reaction, $\Delta H$ is the difference in the enthalpy of the chemical reaction, $\Delta S$ is the difference in the entropy of the chemical reaction, is the reaction temperature ($T = C+273.15$, Kelvin), $C_p$ is the molar heat capacity of the substance at 298K.
According to thermodynamic principles, when the gibbs free energy change value of a chemical reaction under a certain condition is negative, the chemical reaction will proceed spontaneously under this condition. Table 4 lists the enthalpy and entropy of the products and reactants involved in the continuous chemical reaction that may occur at the interface of the layered material layer at 298K. According to formula (4), the reaction equations (1) and (2) at 2098K are calculated. And (3) Gibbs free energy, in order to determine the possibility of chemical reaction of the material at the process molding temperature.

### Table 4 Enthalpy and entropy of chemical reactants

| materials | S (J·K⁻¹·mol⁻¹) | H (kJ·mol⁻¹) | Cp (J·K⁻¹·mol⁻¹) |
|-----------|----------------|--------------|------------------|
| Mo        | 23.96          | 0            | 22.93+5.44×10⁻³T|
| Si₃N₄     | 112.97         | -744.75      | 76.34+109.04×10⁻³T-6.54×10⁵T⁻² |
| MoSi₂     | 65.02          | -131.71      | 67.83+11.97×10⁻³T-6.57×10⁵T⁻² |
| Mo₅Si₃    | 207.34         | -309.62      | 183.36+35.04×10⁻³T-12.00×10⁵T⁻² |
| Mo₃Si     | 106.15         | -116.40      | 85.84+22.68×10⁻³T-0.32×10⁵T⁻² |
| N₂         | 191.5          | 0            | 27.86+4.27×10⁻³T |

The Gibbs free energy calculation results of the chemical reaction formula of the Si₃N₄/Mo layered composite material can be seen in Table 5. From the calculation results in the table, it can be seen that the Gibbs free energy of each formula is negative. From this we can judge that the reaction formulas (1), (2) and (3) can proceed spontaneously at room temperature. This proves that at a sintering temperature of 1800°C, Si₃N₄ and Mo will undergo a chemical reaction to form MoSi₂, Mo₅Si₃, and Mo₃Si. And, because the Gibbs free energy of formula (2) is smaller, this reaction will occur more easily, which also proves that Mo₅Si₃ generates the largest proportion of intermetallic molybdenum-silicon compounds in the metal layer.

### Table 5 Gibbs free energy of friction chemical reaction

| chemical equation                      | ΔG 2098K (kJ·mol⁻¹) |
|----------------------------------------|---------------------|
| 3Mo + 2Si₃N₄ → 3MoSi₂ + 4N₂             | -255.21             |
| 20MoSi₂ + 48Mo → Mo₃Si + 13Mo₅Si₃       | -1873.38            |
| Mo₅Si₃ + 48Mo → 3Mo₃Si                  | -21.54              |

3.5 Tribological properties

Under different loads, the friction coefficient results of Si₃N₄ and Si₃N₄/Mo layered composites and TC4 pairs are shown in Fig. 7. When the load of the friction pair increases, the friction factor shows a certain upward trend. Moreover, in the same
lubricating environment, the friction coefficient of the 9Si₃N₄-Mo/TC4 friction pair is slightly higher than that of the 11Si₃N₄-Mo/TC4 friction pair and Si₃N₄/TC4. On the other hand, from the wear of the Si₃N₄/Mo and TC4 friction pair in Fig. 8, it can be seen that the wear rate of the layered material pin sample is in the order of 10⁻⁵ mm³/(N·m), and the wear rate of the titanium alloy disc sample is in the order of 10⁻³ mm³/(N·m). In addition, the signal wear rate and total wear rate of 11Si₃N₄-Mo/TC4 friction pair are lower than 9Si₃N₄-Mo/TC4 friction pair, indicating that the tribological properties of 11Si₃N₄-Mo/TC4 are slightly better than 9Si₃N₄-Mo/TC4.

---

**Fig. 7** Friction factor a of friction pairs under different loads in artificial seawater

**Fig. 8** Wear rate of friction pairs under different loads in artificial seawater
Fig. 9 shows the wear morphology of 11Si₃N₄-Mo ceramic pins in seawater with different loads. Under different loads, the surface of the laminated ceramic pin specimens all adhered. By comparing the micro morphology of the ceramic pins in Fig. 9, it can be found that as the load increases, the degree of substance adhesion gradually increases. Perform EDS energy spectrum analysis on the three zones: "A", "B" and "C" in Fig. 9(c), and the results are shown in Fig. 10. The EDS test results show that the A zone mainly contains Si element, which characterizes this area as a ceramic matrix; the B zone contains Si, Mo, Ti, V and other elements. Among them, Mo element is a layered material. In the metal interlayer, the Si element may come from the formed molybdenum silicon compound or the wear debris of the ceramic matrix. The Ti and V elements come from the TC4 disc of the auxiliary material; the elements contained in the C zone are lacks Mo element compared with the B zone, which indicates that this area is mainly from the TC4 disc. The wear morphology of the TC4 disc paired with the 11Si₃N₄-Mo pin sample is shown in Fig. 11. It can be found from the picture that there are a large number of trench ploughs on the wear surface of the TC4 disc, and as the load increases, the wear surface of the TC4 disc became more and more rough. Therefore, it can be concluded that the friction mechanism of Si₃N₄-Mo/TC4 is a mixed wear of adhesive wear and abrasive wear.
Fig. 9 The friction surface morphology of $11\text{Si}_3\text{N}_4$-Mo pin sample in artificial seawater under different loads: (a) 10N; (b) 20N; (c) 30N.

Fig. 10 The analysis results of the friction surface of $11\text{Si}_3\text{N}_4$-Mo pin sample under a load of 30N: (a) A zone; (b) B zone; (c) C zone.
Fig. 11 The friction surface morphology of TC4 mating against 11Si3N4-Mo pin sample in artificial seawater under different loads: (a)10N, (b)20N, (c)30N

4. Conclusions

In the present study, by adding Mo as metal interlayers to Si3N4, Si3N4-Mo laminated ceramic composite with a layered structure was prepared via hot-pressing at 1800°C. The laminated structure and Interface composition of Si3N4-Mo laminated ceramic composite on the physical, mechanical and friction behavior were investigated. The findings obtained in this work can be summarized as follows:

(1) The multilayer structure could improve the fracture toughness of Si3N4-Mo laminated composites compared with pure Si3N4. And the internal stress generated by the difference in thermal expansion coefficient hinders the propagation of cracks at the layer interface.

(2) The main material present at the interface of the Si3N4-Mo layered composite layer is the molybdenum silicides. it is speculated that the material distribution
from the interface of the Si$_3$N$_4$-hBN/Mo layered composite layer to the center of the metal layer is Si$_3$N$_4$→ MoSi$_2$→ Mo$_5$Si$_3$→ Mo$_3$Si→ Mo, and Mo$_5$Si$_3$ produces the largest proportion of intermetallic molybdenum silicides in the metal layer.

(3) The friction mechanism of Si$_3$N$_4$-Mo/TC4 in artificial seawater is a mixed wear of adhesive wear and abrasive wear. And with the increase of the load, the tribology properties of Si$_3$N$_4$-Mo laminated ceramic composite decreased.

(4) When the content of Mo in the layer structure is higher, it is beneficial to hinder the diffusion of cracks and improve the fracture toughness of the material. But with the lower content of Mo, Si$_3$N$_4$-Mo laminated ceramic composite had better tribology properties.

Acknowledgements

This study was supported by the Open Fund of National Joint Engineering Research Center for abrasion control and molding of metal materials (HKDNM201902) and Shaanxi Provincial Department of Science and Technology Science and Technology Project (2018JM5056).

Reference:

[1] Wang LJ, Qi Q, Cai P, et al. New route to improve the fracture toughness and flexural strength of Si3N4 ceramics by adding FeSi$_2$. Scripta Mater 2017, 123: 11-14.

[2] Klemm H. Silicon Nitride for High-Temperature Applications. Journal of the American Ceramic Society 2010, 93: 1501-1522.

[3] Smith BL, Schäffer TE, Viani M, et al. Molecular mechanistic origin of the toughness of natural adhesives, fibres and composites. Nature 1999, 399: 761-763.

[4] Clegg WJ, Kendall K, Alford NM, et al. A simple way to make tough ceramics. Nature 1990, 347: 455-457.

[5] Kovar D, Thouless MD, Halloran JW. Crack Deflection and Propagation in Layered Silicon Nitride/Boron Nitride Ceramics. Journal of the American Ceramic Society 1998, 81: 1004-1112.

[6] Zan QF, Wang CA, Huang Y, et al. Effect of geometrical factors on the mechanical properties of Si$_3$N$_4$/BN multilayer ceramics. Ceramics International 2004, 30: 441-446.

[7] Jun T. Study on preparation and properties of B$_4$C/BN laminates. hesis, M.D. Thesis. Jingdezhen (China): Jingdezhen Ceramic Institute, 2008.

[8] Zuo KH, Jiang DL, Lin QL, et al. Improving the mechanical properties of Al$_2$O$_3$/Ni laminated composites by adding Ni particles in Al$_2$O$_3$ layers. Materials Science and Engineering: A 2007, 443: 296-300.

[9] Chen W, Zhang D, Lv ZL, et al. Self-lubricating mechanisms via the in situ
formed tribo-film of sintered ceramics with hBN addition in a high humidity environment. International Journal of Refractory Metals & Hard Materials 2017, 66:163-173.

[10] Chen W, Wang K, Gao YM, et al. Investigation of tribological properties of silicon nitride ceramic composites sliding against titanium alloy under artificial seawater lubricating condition. International Journal of Refractory Metals & Hard Materials 2018, 76:204-213.

[11] Chen W, Wang ZX, Gao YM, et al. Microstructure, mechanical properties and friction/wear behavior of hot-pressed Si₃N₄/BN ceramic composites. Ceramics-Silikaty 2019, 63:1-10.

[12] Zhang CS, Liu Q, Chen W. Effect of hBN content on property and microstructure of Si₃N₄-hBN composite ceramics. Journal of Inorganic Materials 2017, 32: 509-512.

[13] Chen W, Zhang D, Ai X. Effect of load on the friction and wear characteristics of Si₃N₄-hBN ceramic composites sliding against steels. Ceramics International 2017, 43: 4379-4389.

[14] Chen W, Shi HX, He NR, et al. Friction and wear properties of Si₃N₄-hBN ceramic composites using different synthetic lubricants. Ceramics International 2018, 44: 16799-16808.

[15] Zhang D, Chen W, Ai X, et al. Effect of the humidity on the friction and wear characteristics of Si₃N₄-hBN composite ceramics. Proceedings of the Institution of Mechanical Engineers Part J-Journal of Engineering Tribology 2017, 231:1517-1526.

[16] Chen W, Gao YM, Liang C, et al. Influence of Sliding Speed on the Tribological Characteristics of Si₃N₄-hBN Ceramic Materials. Tribology Transactions 2013, 11: 687-696.

[17] Zuo KH, Jiang DL, Lin QL, et al. Improving the mechanical properties of Al₂O₃/Ni laminated composites by adding Ni particles in Al₂O₃ layers. Materials Science and Engineering: A 2007,443:296-300.

[18] Yoon JK, Lee JK, Lee KH, et al. Microstructure and growth kinetics of the Mo₅Si₃ and Mo₃Si layers in MoSi₂/Mo diffusion couple. Intermetallics 2003, 11:687-696.

[19] Li YF, Xiao B, Wang GL, et al. Revealing the novel fracture mechanism of the interfaces of TiB₂/Fe composite from a first principles investigation. Acta Materialia 2018, 156: 228-244.

[20] Li YF, Ding YC, Xiao B, et al. Anisotropic electrical and lattice transport properties of ordered quaternary phases Cr₂TiAlC₂ and Mo₂TiAlC₂: A first principles study. Physics Letters A 2016,380:3748-3755.