

Wear protection by in-situ forming amorphous-nanocrystalline composite layer through friction-induced self-reaction

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Abstract: This study proposes a novel wear protection strategy that focuses on the in-situ construction of an amorphous-nanocrystalline composite layer via friction-induced mechanochemical reactions. To realize this concept, a multicomponent $(\text{FeSiB})_x\text{Cu}_y$ (at.%) alloy was selected as the precursor material. Subsequently, sliding wear tests were conducted under distinct normal loads (10 N and 30 N) to control the input of mechanical energy. Under the higher load, an amorphous-nanocrystalline composite structure was formed, with nanocrystalline Cu embedded in an Fe-Si-B-O amorphous matrix, indicating the incorporation of environmental O into the tribological layer during sliding. This composite layer significantly improved the wear resistance by the synergistic plastic deformation mechanisms during sliding contact.

Key words: wear protection; in-situ; tribological layer; amorphous-nanocrystalline

1 Introduction

Wear-related energy losses and component damage, including friction and remanufacturing of components that failed by wear contacts, account for 23% of global energy consumption with an estimated cost exceeding 2500 Billion Euros per year [1]. Thus, many efforts [2-4] have been devoted to investigating wear mechanisms. Results demonstrate that wear behaviors are highly dependent on service

conditions and material properties, where the primary mechanisms involve abrasion, adhesion, fatigue, and oxidation. Regardless of the specific mechanism, the essence of material removal lies in local contact stress exceeding the material's corresponding strength. Consequently, various surface strengthening strategies, including plasma spraying [5], electroplating/electroless deposition [6, 7], hardfacing [8], and magnetron sputtering [9], have been proposed to develop wear-resistant metallic materials.

Among these approaches, amorphous alloys (or metallic glasses), with strength and elasticity surpassing those of conventional structural alloys, have caught considerable attention in recent years [10]. For instance, Yuan et al. [11] fabricated Fe-based or Al-based amorphous coatings with enhanced yield strengths ($\sigma_y \sim E/50$, where E denotes the elastic modulus) via flame spraying, plasma spraying, laser cladding, and other coating technologies. These amorphous coatings exhibited significantly lower wear rates than their corresponding crystalline counterparts [12-14]. Amorphous coatings are prone to peeling or cracking. This tendency is primarily attributed to substantial differences in physical properties between the coatings and their substrates. Furthermore, their high hardness creates challenges for subsequent machining—particularly for high-precision contact-moving components. Given these limitations, ongoing research remains necessary to advance the practical application of amorphous coatings.

As is well known, friction usually induces the formation of a tribological layer at the interface through mechanochemical reactions, providing an advantage in wear

resistance [15, 16]. Such a tribological layer is essentially a self-organizing and self-adaptive surface structure formed under external loading and continuous shear. During this process, the friction interface can dynamically regulate its tribological state through material transfer, third-body evolution, and the formation of secondary tribo-layers, thereby stabilizing the interface and reducing wear [17]. In addition, superlubricity achieved via frictional self-reaction or structural self-adaptation has also been widely adopted as an innovative route for friction reduction [18, 19]. Recent investigations [20, 21] have further demonstrated that an amorphous structure can be formed on the surfaces of specific materials under critical frictional conditions. In comparison to traditional amorphous coating technologies, this in-situ method, characterized by a self-organizing and self-adaptive process, can avoid subsequent machining challenges. More importantly, this method often induces the formation of nanocrystalline structures in the subsurface, driven by the gradient distribution of contact stress along the depth direction [22]. This amorphous-nanocrystalline gradient structure, in turn, significantly enhances interfacial bonding strength. However, the plastic deformation of amorphous regions is typically localized within shear bands, which results in the generation of cracks and brittle wear debris upon wear, thus evoking a micro-cutting mechanism that readily diminishes its inherent wear-resistant advantages [23, 24]. To address this brittle issue, introducing a ductile crystalline phase to enable homogeneous plastic deformation has been widely applied for toughening bulk amorphous materials. For example, Gao et al. [25] investigated the effects of Cu addition on the toughness of Ti/Zr-based bulk amorphous materials, and

the resulting amorphous-crystalline dual-phase composites exhibited an elongation at break as high as 13%.

Inspired by these findings, this study proposes a novel wear protection concept—the in-situ construction of a dual-phase composite coating, based on precursor materials design and the evolution of surface microstructures driven by mechanochemical reactions. This dual-phase composite coating, featuring dispersed nanostructures embedded within an amorphous matrix, is anticipated to outperform conventional coatings with an amorphous-nanocrystalline gradient distribution. Furthermore, to clarify the self-organization process of the coating and its corresponding wear-resistant mechanisms, a comprehensive investigation was conducted on the evolution of microstructures.

2 Experimental materials and methods

2.1 Precursor materials design and preparation

Precursor materials in this study were primarily used to form an amorphous-crystalline composite structure on their surfaces by friction-induced mechanochemical reactions. However, the amorphization process is highly challenging and requires extreme thermodynamic conditions. For instance, many recent studies [26, 27] have demonstrated that alloys featuring multicomponent compositions, large negative enthalpy of mixing, and appreciable atomic-size mismatch are favorable for obtaining strong glass-forming ability. Furthermore, amorphization necessitates overcoming a certain energy barrier to achieve disordered atomic arrangement. In other words, only specific material systems are suitable for this purpose, and the testing conditions need

to be well matched as well.

According to the empirical criterion for the formation of amorphous materials [26-28], a multicomponent $(\text{FeSiB})_x\text{Cu}_y$ (at.%) alloy was selected as the precursor material. Environmental oxygen (O) was not an initial alloying element but could be incorporated into the tribological layer during sliding. Iron (Fe), silicon (Si), boron (B), and environmental O possess a large negative mixing enthalpy and atomic radius difference—a characteristic that enhances the alloy's glass-forming ability, whereas copper (Cu) was primarily employed to facilitate the formation of a crystalline structure due to its positive mixing enthalpy (13 kJ/mol) with Fe, as shown in Figs. 1(a-b). Three precursor materials with compositions of $\text{Fe}_{80}\text{Si}_{10}\text{B}_{10}$, $(\text{Fe}_{80}\text{Si}_{10}\text{B}_{10})_{95}\text{Cu}_5$ and $(\text{Fe}_{80}\text{Si}_{10}\text{B}_{10})_{90}\text{Cu}_{10}$ —were prepared and designated as S0, S5, and S10, where the numerical values correspond to the Cu content in the composition. The Fe-Si-B atomic ratio of 8:1:1 was chosen based on our preliminary studies and repeated trials to obtain as-sintered bodies that are dense and essentially defect-free. Meanwhile, varying the Cu content was intended to investigate its effects on the formation of the desired ductile crystalline phase within an amorphous tribological layer.

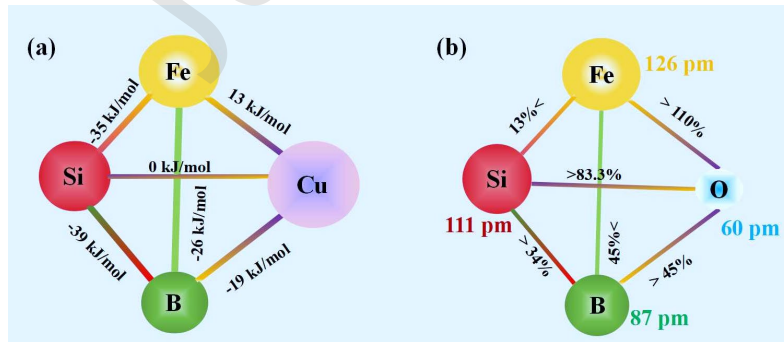


Fig. 1 The design principles of precursor materials used in this study: (a) mixing enthalpy; (b) atomic radius difference.

Figs. 2(a-b) illustrate the preparation procedures of precursor materials used in this study. The elemental Fe, Si, B, and Cu powders were purchased from Beijing Yanbang New Material Technology Co., Ltd., with a purity of 99.95% and particle sizes ranging from 45 to 100 μm . As shown in Fig. 2(a), these powders were first blended in a planetary ball mill (DECO-PBM-AD-10L) under an Ar atmosphere prior to hot-press sintering. Stainless steel balls with diameters of 10, 8 and 5 mm were used as the milling media, and their mass ratio was 2:1:2. The ball-to-powder weight ratio, rotational speed, and milling time were 10:1, 400 rpm, and 2 h, respectively. After ball milling, the mixed powders were loaded into a graphite die for subsequent vacuum hot-press sintering. Detailed information regarding the sintering process is presented in Fig.2(b): the chamber was evacuated to < 20 Pa using a mechanical pump, followed by further evacuation to $< 10^{-3}$ Pa with a diffusion pump; a preload of 5 MPa was applied for 5 min before heating; the pressure was then increased to 30 MPa and maintained throughout the sintering process; the temperature was raised at a rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to $850\text{ }^{\circ}\text{C}$, held isothermally for 120 min, cooled to $200\text{ }^{\circ}\text{C}$ at $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, and finally furnace-cooled to room temperature under vacuum. The as-sintered disk specimens had a dimension of $\text{O}30 \times 10\text{ mm}$.

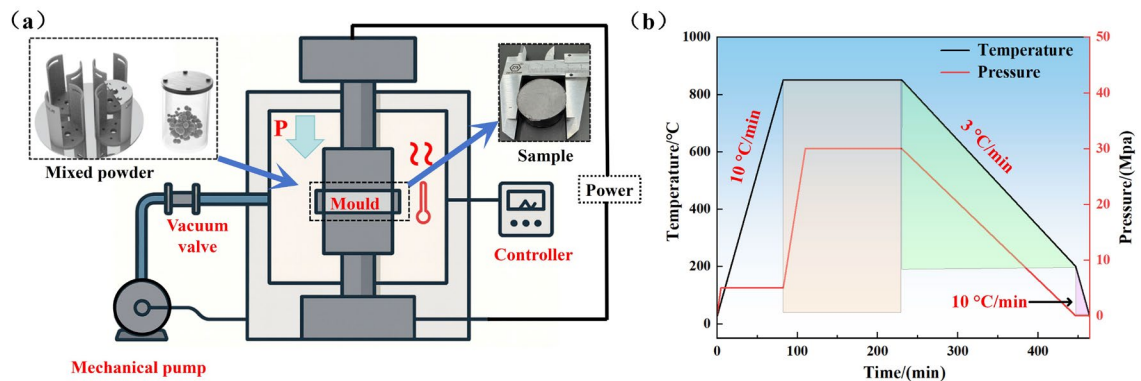


Fig. 2 Schematic illustration of the vacuum hot-press sintering process (a), and corresponding technological procedures (b).

2.2 Materials characterization

To better understand the microstructural evolution, the microstructural features of different samples before and after sliding wear tests were examined by a scanning electron microscope (SEM, Zeiss SUPRA 55), an optical microscope (OM, ZEISS Axiovert 40 MAT), and a transmission electron microscope (TEM, JEM ARM300F2). Samples for TEM observation were fabricated using a focused ion beam (FIB) technology. Compositional and phase analyses were performed using energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and selected-area electron diffraction (SAED), respectively. To study the effects of mechanical properties on tribological performances, the hardness was measured by a Rockwell hardness tester (HRTS-150Z) according to the relevant ASTM standard. The measurements were conducted using the HRC scale with a diamond cone indenter under a total load of 150 kgf. The dwell time for each indentation was 15 s at room temperature (25 ± 1 °C). For each sample, five hardness measurements were taken at different positions, and the average value was used for analysis. Simultaneously, cylindrical specimens with a diameter of 5 mm and a height of 5 mm were used for the compression tests. The quasi-static compression tests were carried out at room temperature (25 ± 1 °C) using an electronic universal testing machine (Zwick/100 kN Allround floor Z100SH). The specimens were compressed at a crosshead speed of 0.5 mm/min, corresponding to an initial strain rate of

approximately $1.67 \times 10^{-3} \text{ s}^{-1}$. Three repeated compression tests were conducted for each sample to ensure data reliability, and the results are reported as mean values. After wear tests, the worn surface morphology and composition were examined to identify the wear mechanisms by using SEM and EDS, respectively.

2.3 Wear tests

Figs. 3(a-c) provide the wear testing schematic diagram and operating conditions. A reciprocating ball-on-disk tribometer (MFT-50 Rtec Instruments) was used to evaluate the tribological performances of the as-sintered samples. Unlubricated reciprocating sliding tests were conducted at room temperature ($25 \pm 1 \text{ }^{\circ}\text{C}$), with a relative humidity of 50%. Prior to friction, the testing surface of each sample was ground with SiC sandpapers (#180-#3000) to a roughness of $R_a \approx 0.6 \text{ }\mu\text{m}$. A GCr15 steel ball with a diameter of 6 mm was selected as the counterpart. The tests were conducted under two distinct normal loads of 10 N and 30 N, with a one-way stroke length of 10 mm. The average sliding speed was 0.2 m/s and the total sliding distance was 360 m. The different load conditions were used to vary the driving force of mechanochemical reactions at the tribological interface. During each test, the friction coefficient was continuously monitored. For each material condition, the test was repeated three times to ensure the reliability of the experimental data.

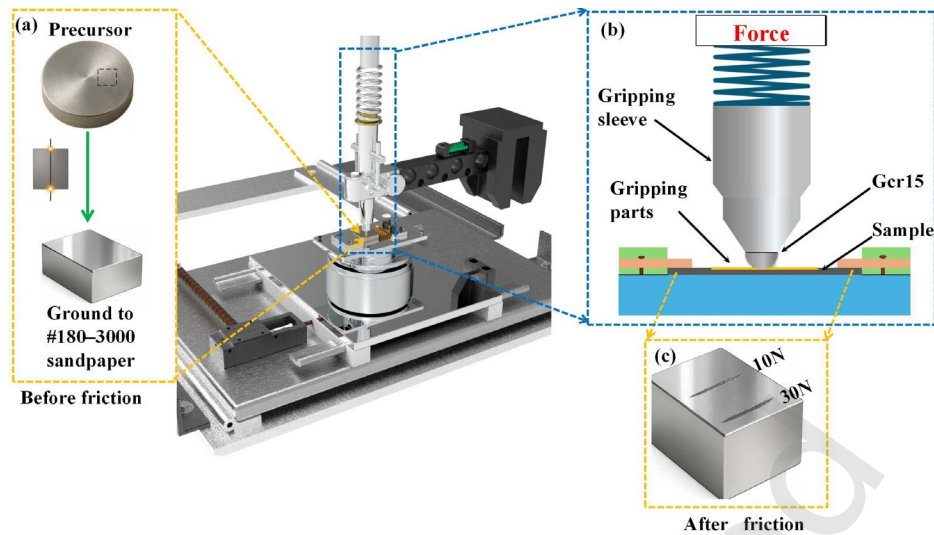


Fig. 3 Wear testing schematic diagram and operating parameters applied in this study: (a) pretreatment of the samples surfaces; (b) the schematic diagram of the experimental device; (c) the illustration of wear tracks.

After the wear tests, the wear performance was evaluated by measuring material volume loss using a 3D white-light interferometer (Bruker Contour GT-K1). The wear volume was calculated by integrating the net material loss of the wear scar with reference to the unworn surface plane. The pile-up ridges along the wear track edges were attributed to plastic displacement instead of actual material removal, and thus excluded from the net wear volume calculation. In order to reveal the wear mechanisms, the worn surface morphology and elemental distribution maps were obtained by using SEM and EDS technologies, respectively. Subsurface cross-sections along the normal-direction/sliding-direction (ND-SD) plane were prepared by FIB and examined by SEM and TEM. Electron-transparent lamellae beneath the worn surface were lifted out by FIB using a standard procedure and characterized by TEM at an accelerating voltage of 200 kV.

3 Results and discussion

3.1 Microstructural features and mechanical properties

Fig. 4 displays the XRD patterns of the as-sintered precursor materials (S0-S10). It can be clearly observed that the phase composition of all samples is dominated by two characteristic phases: α -Fe solid solution and iron boride (Fe_2B), which are well-documented as typical equilibrium phases in Fe-Si-B system alloys [29-31]. To further clarify the formation mechanism of the α -Fe solid solution, Zhang et al. [32] conducted systematic investigations on the crystallization behavior of Fe-based amorphous alloys. Their findings indicated that the α -Fe solid solution forms through the diffusion of Si atoms and the Fe_3Si phase into the α -Fe lattice. Consistent with this mechanism, the (110) diffraction peak of α -Fe in the present XRD results ($2\theta = 44.876^\circ$) exhibits a slight shift toward a higher angle as compared to the standard peak position ($2\theta = 44.67^\circ$), which reveals a reduced interplanar spacing. Relatively weak diffraction peaks at $2\theta=36.9^\circ$ and 43.23° are respectively assigned to the (310) and (002) planes of Fe_2B , indicating the formation of a very minor boride phase. This is in agreement with the findings of Ref. [31], where the Fe_2B formation was determined to occur within the temperature range of 496-901 °C. With the increasing Cu content in S5 and S10, additional diffraction peaks corresponding to crystalline Cu appear and intensify, whereas the intensity of the Fe_2B peaks gradually decreases. This observation implies that the added Cu mainly exists in the form of crystalline Cu phases and simultaneously suppresses the formation of Fe_2B . In contrast, the positions and full width at half maximum of α -Fe diffraction peaks remain essentially

unchanged, which reflects extremely low solubility of Cu atoms in the α -Fe matrix and thus negligible effects on the lattice structure. Furthermore, it is noteworthy that no obvious amorphous hump or diffuse scattering is detected in the background of the XRD patterns, confirming that all as-sintered precursor samples achieve complete crystallization as required.

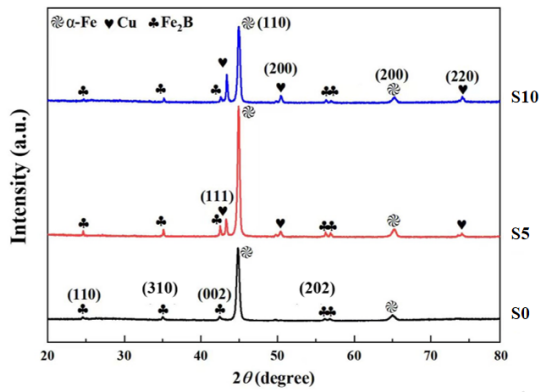


Fig. 4 XRD patterns of all as-sintered precursor materials

Figs. 5(a–g) provide the microstructural features and phase information of the as-sintered samples S0–S10. It can be seen that sample S0 is mainly composed of two distinct phases: the α -Fe matrix and the Fe_2B phase. This phase constitution is verified by the corresponding EDS and crystallographic analyses in Figs. 5(d) and 5(e), consistent with the XRD results shown in Fig. 4. The bulk Fe_2B phases with a size of about several micrometers are observed to be embedded uniformly within the α -Fe matrix. Figs. 5(b) and (c) illustrate the microstructures of samples S5 and S10, respectively. It is observed that the added Cu element primarily precipitates in the form of bulk crystalline phases, which is consistent with our preliminary expectation. This phenomenon can be explained by the strong crystallization tendency of Cu, which results from its positive mixing enthalpy (+13 kJ/mol) with Fe [33, 34]—a

thermodynamic characteristic that promotes the nucleation and growth of crystalline Cu. Additionally, the Cu crystals are clearly distributed around the Fe₂B phases; this distribution may exert a certain inhibitory effect on the formation and growth of Fe₂B phases. This inference can be supported by the XRD patterns in Fig. 4, where the diffraction intensity of Fe₂B peaks gradually decreases with the increase in Cu content. To further clarify the phase structures and interfacial characteristics, three representative regions, namely 1-Area (①) in Fig. 5(a), and 2-Area (②) and 3-Area (③) in Fig. 5(c), were selected for TEM and HRTEM analyses. Specifically, 1-Area was selected to identify the α -Fe/Fe₂B phases in S0, whereas 2-Area and 3-Area were used to characterize the Fe₂B/Cu and Cu/ α -Fe interfaces in S10, respectively. Figs. 5(d) and (e) provide the bright field image and corresponding high-resolution image of 1-Area in Fig. 5(a), revealing the body-centered cubic (BCC) structured α -Fe matrix and body-centered tetragonal (BCT) structured Fe₂B. As a typical hard and brittle intermetallic phase, Fe₂B contributes significantly to the enhancement of matrix strength through a dislocation pinning effect—effectively hindering the motion of dislocations during plastic deformation [31, 32]. However, the incoherent interface between Fe₂B and α -Fe may cause negative effects on the toughness of materials. Figs. 5(f) and 5(g) show the high-resolution images corresponding to 2-Area and 3-Area of Sample S10, respectively. Better interfacial matching is observed at both the Fe₂B/Cu and Cu/ α -Fe interfaces. This feature is beneficial for improving deformation compatibility.

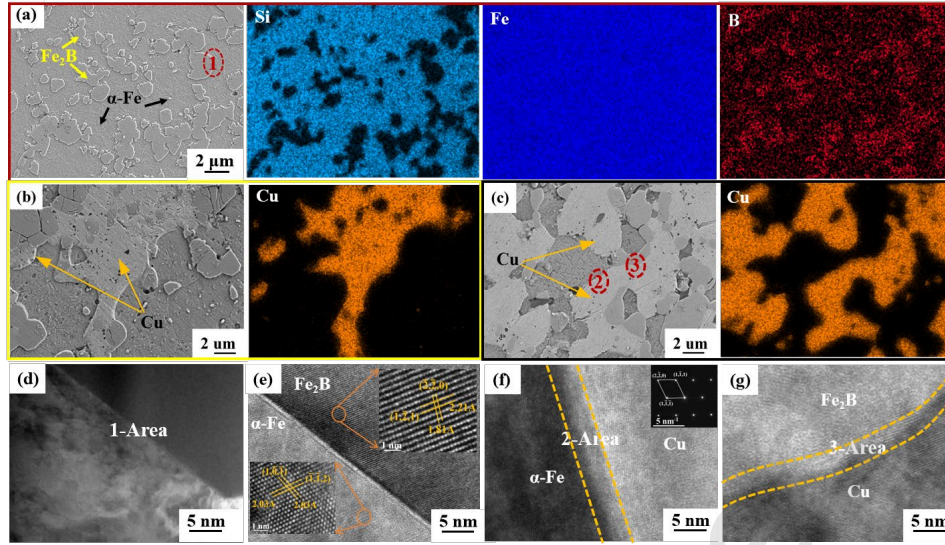


Fig. 5 Microstructural features of the as-sintered samples S0, S5, and S10: (a) SEM image of S0 and the corresponding elemental distributions; (b) SEM image of S5 and the Cu distribution; (c) SEM image of S10 and the Cu distribution; (d) bright-field TEM image of 1-Area in (a); (e) corresponding HRTEM image of 1-Area; (f) HRTEM image of 2-Area in (c); (g) HRTEM image of 3-Area in (c).

Table 1 summarizes the mechanical properties of the different samples. With increasing Cu content, the hardness and compressive strength decreased, whereas the fracture strain increased. To further clarify the deformation behavior, the fracture morphologies after compression tests were examined. As shown in Figs. 6(a) and 6(a1), S0 exhibits relatively flat shear facets accompanied by obvious microcracks, indicating a strong tendency toward brittle fracture. In contrast, S10 exhibits a rougher and more irregular fracture surface with pronounced shear-deformation traces, as shown in Figs. 6(b) and 6(b1). Together with the increase in fracture strain from $3.4 \pm 0.15\%$ for S0 to $8.7 \pm 0.16\%$ for S10, these morphological features indicate that Cu addition enhances the plastic deformation capability and reduces the susceptibility to

brittle fracture. The elemental distributions in Fig. 6(b2) further confirm the presence of Cu-rich regions in S10.

Table 1 Mechanical properties of different samples

Mechanical properties Samples	Yield strength (MPa)	Compression strength (MPa)	Hardness (HRC)	Fracture strain (%)
S0	1451 ± 10.32	2107 ± 8.96	48 ± 0.54	3.4 ± 0.15
S5	1142 ± 8.17	1822 ± 6.54	42 ± 0.72	7.6 ± 0.23
S10	1038 ± 9.28	1448 ± 10.92	38 ± 0.69	8.7 ± 0.16

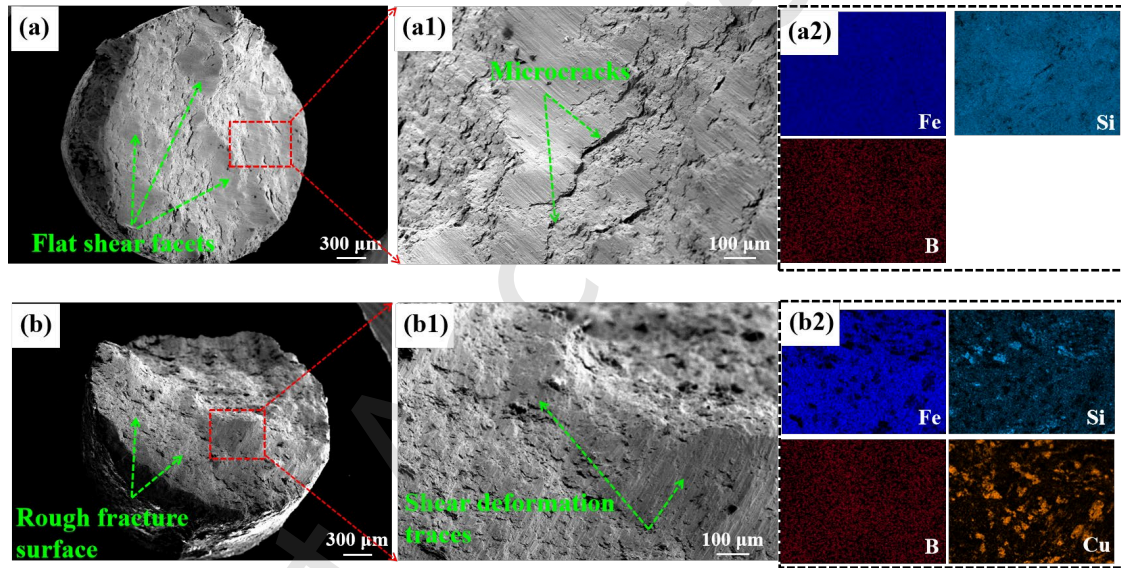


Fig. 6 Fracture morphologies of S0 and S10 after compression tests: (a) macroscopic fracture morphology of S0; (a1) magnified view of the region marked in (a); (a2) corresponding elemental distributions of (a1); (b) macroscopic fracture morphology of S10; (b1) magnified view of the region marked in (b); (b2) corresponding elemental distributions of (b1).

3.2 Friction performances

Figs. 7(a) and 7(b) show the evolution of friction coefficients (COFs) of different samples throughout the entire sliding wear tests, as well as the average COF values calculated for the steady-state period. It can be seen that the COF for each sample

increases significantly within the very short running-in stage. This behavior has been widely reported and is generally attributed to the gradual establishment of conformal contact between the friction pairs, which consequently increases the real contact area [35, 36]. In addition, the duration of the running-in stage varies with both the sample composition and applied normal load. This may be explained by the surface deformation behavior of materials. S0, which does not contain a ductile Cu phase, usually possesses a higher deformation resistance and higher work hardening ability, which effectively reduces the viscoelastic hysteresis during the establishment process of conformable contact [36]. As a result, S0 exhibits a shorter running-in stage compared with S5 and S10. This also explains the longer running-in stage observed under the higher normal load of 30 N, as shown in Fig. 7(b).

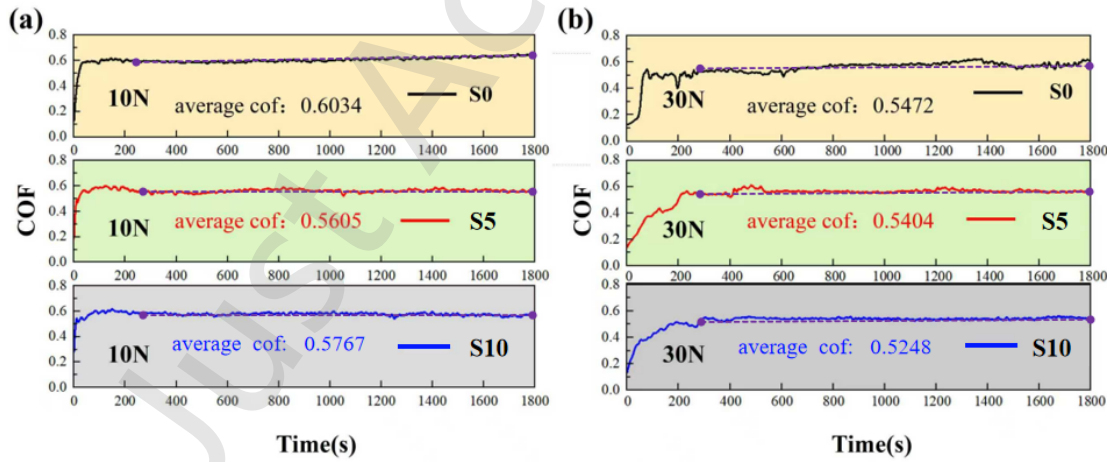


Fig. 7 Friction coefficient evolution and average steady-state friction coefficients of the studied samples under different loads: (a) 10 N; (b) 30 N.

As the friction process continues, an interesting yet abnormal phenomenon in the present study is presented: after the short running-in period, the COFs of S5 and S10 stabilized at constant levels, whereas S0 exhibited a slight secondary increasing trend.

Undoubtedly, the addition of Cu was the primary factor responsible for this behavior. According to previous studies [37, 38], ductile crystalline Cu can promote the formation of a friction film, which is beneficial to obtain stable friction performance. In addition, the friction fluctuation of S10 throughout the whole sliding duration is less significant than that of S0 and S5. Previous studies [2, 39] have shown that friction fluctuations are closely related to worn-surface morphology and interfacial contact conditions, which can be affected by microstructural homogeneity, microhardness, strain hardening, thermal softening, oxide debris, glaze layers, and surface cracking. Accordingly, this specific friction behavior will be further discussed in subsequent sections.

With increasing applied load, the average steady-state COF exhibited a decreasing trend. Similar results have been widely documented in previous literature [3, 39]. According to Coulomb's law, an increase in normal load should increase the friction force [2]. However, if the compressive stress simultaneously increases the real contact area between friction pairs disproportionately, the final friction force per unit area will decrease instead. Under both load conditions, the Cu-containing samples (S5 and S10) exhibited lower average friction coefficients than S0. Similar effects of Cu addition on friction performance have also been investigated in previous studies [38, 40]. In addition, some previous studies [41-43] suggested that changes in microstructure and mechanical properties induced by Cu addition may also influence friction behavior, with higher hardness being associated with a lower friction coefficient in some cases. To examine whether this relationship applies to the present system, the hardness of the

samples was evaluated. The results indicated that the hardness decreased with increasing Cu content (S0: HRC 48 ± 0.54 ; S5: HRC 42 ± 0.72 ; S10: HRC 38 ± 0.69), owing to the introduction of relatively soft Cu-rich phases, while the friction coefficient did not increase accordingly. This indicates that the friction behavior in the present system cannot be simply explained by bulk hardness. Instead, the reduced friction coefficient is more closely associated with the formation and evolution of the Cu-containing tribological layer during sliding [38, 40], which provides a lubricating effect and is further discussed in the following sections.

3.3 Wear performances

Figs. 8(a-d) illustrate the wear behaviors of the samples under different load conditions, as well as the corresponding characteristics of their wear tracks. As shown in Fig. 8(a), the variations in the wear track depths of S0 with loads are reflected by the color gradient columns on the right. At a low applied load of 10 N, the wear track exhibits an average width of approximately 1.0 mm and a maximum depth of about 26 μm . When the load increases to 30 N, the track width and depth rise to 1.1 mm and 42 μm , respectively. This clearly indicates that the wear rate escalates significantly with increasing load, which is further verified by the data collected in Fig. 8(d). This indicates that the increased contact stress led to severe plastic deformation and consequent material removal [2, 3]. Two distinct deformation ridges several micrometers in height are observed along the edges of the wear track, providing further support for this interpretation [3, 44].

Figs. 8(b) and (c) present the cross-sectional profile features of wear tracks for

samples S0-S10 under 10 N and 30 N, respectively. It's apparent that the depth and width of wear tracks for all samples increase with load, as well as the altitude of deformation ridges, all meaning aggravated wear. Besides that, S10 exhibits a relative smooth cross-sectional profile as compared to S0 and S5, regardless of the load conditions. This smoother profile may contribute to the smaller friction fluctuations observed for S10, which is described earlier in Figs. 7(a) and (b). With respect to the wavy feature of wear tracks, previous studies have conducted systematic investigations through worn surface analyses and attributed it to the scratches, inhomogeneous distribution of wear debris, or oxide patches [39, 44].

Fig. 8(d) also exhibits the effects of Cu addition on the wear resistance. It can be seen that S10 has the best wear resistance, followed by S5 and then S0, revealing a positive relation with the Cu content. As is well known, wear performance is strongly dependent on multiple factors, including test conditions, material mechanical properties, surface roughness, and chemical reactions. For this study, the identical factors such as surface roughness and testing conditions can be firstly excluded without doubt. Regarding mechanical properties, our aforementioned test results demonstrate that Cu addition leads to a decrease in hardness (S0: HRC 48 ± 0.54 ; S5: HRC 42 ± 0.72 ; S10: HRC 38 ± 0.69). This observation is particularly interesting, as it deviates from the conventional understanding that higher hardness generally corresponds to lower wear rates [2]. It just goes to show that the chemical reactions happening and the resulting structural evolution at the tribological interfaces played a crucial role. Inevitably, an accompanying transformation of wear

mechanisms should also be taken into consideration. They synergistically compensated the negative influences caused by the reduction in mechanical properties. Even if the load condition was very severe, S10 still possessed an excellent performance. These interpretations are further discussed below in conjunction with the worn-surface analyses.

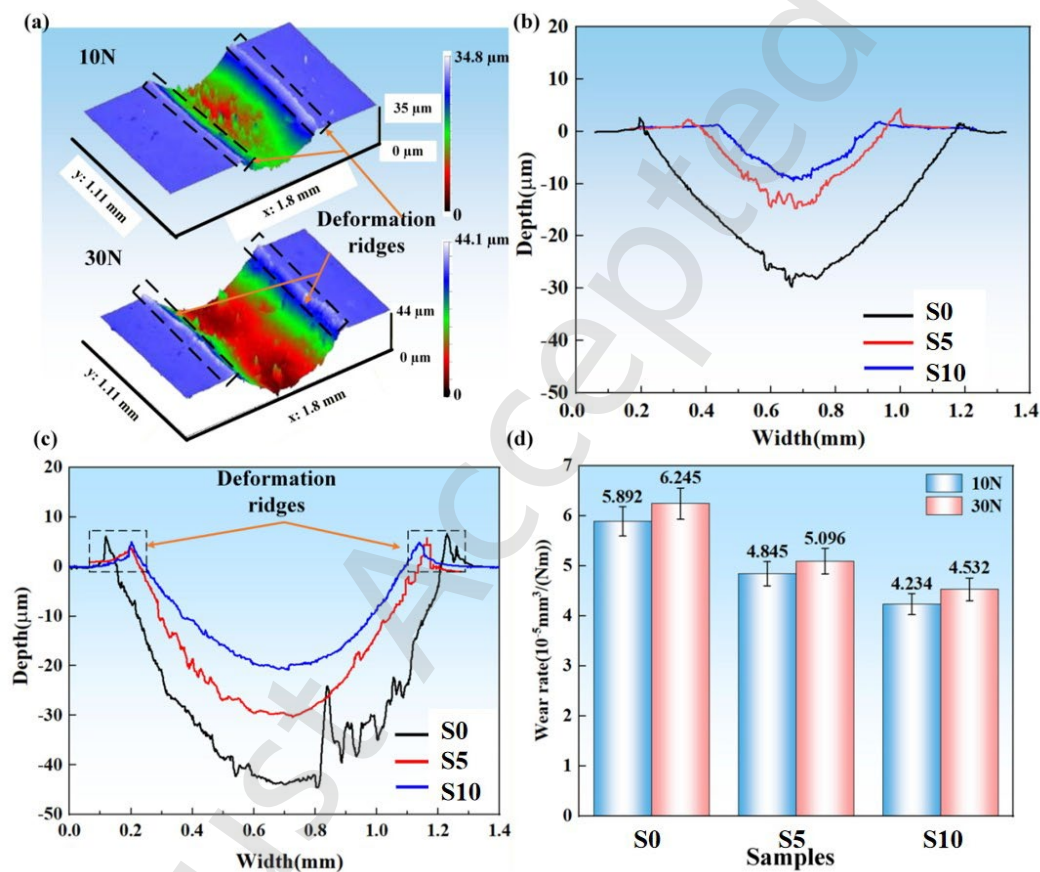


Fig. 8 Wear rates and wear-track features of the studied samples under different loads: (a) 3D wear tracks of S0 under 10 N and 30 N; (b) cross-sectional profiles of wear tracks for samples S0-S10 under 10 N; (c) cross-sectional profiles of wear tracks for samples under 30 N; (d) wear rates of samples under different loads.

3.4 Worn surfaces

Figs. 9(a1-a3) show the worn surface morphologies of S0 under a 10 N load. The

surface presents a high degree of roughness, characterized by obvious patches, cracks, scratches, and wear debris. This is consistent with its cross-sectional profile of wear track in Fig. 8(b), and well explains the friction fluctuation phenomenon in Fig. 7(a). Based on these observations, abrasive wear is identified as the primary mechanism governing the wear performance of S0. As reported in Ref. [15, 45], these patches also known as “secondary contact plateaus”, are formed by compacted wear debris under normal load. The magnified micrograph in Fig. 9(a2) provides partial support for this viewpoint, as it clearly illustrates the as-formed patches and the surrounding wear debris. Regarding crack generation, it was mostly explained by the fatigue behavior during reciprocating sliding [45], and closely related to the material’s microstructure. The scratches were typically caused by the wear debris at the tribological interface with a “three-body abrasion” mechanism [2, 15]. Fig. 9(b1) shows that the worn surface of S5 is significantly smoother than that of S0. Similar morphologies resulting from Cu addition have been widely reported in previous studies [1, 16], which was attributed to the lubricating effect or the formation of a protective tribological layer. The magnified SEM micrograph in Fig. 9(b2) provides further insight into the wear behavior of S5, where distinct plastic deformation and microcracks are observed. This observation indicates a gradual transition in the wear mechanism—from abrasive wear to adhesive wear, driven by the excellent ductility of Cu crystalline phases that alter the mechanical properties of material. To investigate surface spallation and crack initiation on the surface, EDS analyses were conducted simultaneously. First, the results in Fig. 9(b3) demonstrate that O element absolutely participated in the

reconstruction of surface structure, which meets our original design intention. Second, the distribution of different elements corresponding to Fig. 9(b2) shows that microcracks usually initiated in regions without Cu element. On the one hand, this phenomenon indicates the formation of a composite structure with heterogeneous mechanical properties. On the other hand, the Cu-rich region was beneficial to prevent cracks initiation by effective stress release. Figs. 9(c1) and (c2) show the microtopography of worn surfaces for S10, which is characterized by a very smooth appearance. Less cracks and peeling off suggest that the higher Cu content further improved the surface integrity of the material. Moreover, the corresponding EDS results in Fig. 9(c3) demonstrate that a uniformly heterogeneous structure was finally formed. As a result, these features are consistent with the improved wear resistance and more stable friction behavior of S10.

Overall, the Cu addition reduced the hardness of as-prepared materials, but played a positive role in maintaining the surface integrity. This was attributed to its excellent ductility that could reduce microcrack generation during reciprocating friction by stress-strain coordination with hard α -Fe solid solution and Fe_2B , as illustrated in Figs. 11(d-f). As a result, the subsequent third-body abrasive wear caused by the detached hard debris could be effectively suppressed. On the other hand, many studies [46, 47] have demonstrated that ductile constituents within composite friction materials could act as a binder to favor tribological layer formation by improving the agglomeration ability of compacted wear debris, thereby avoiding the direct wear contacts between friction pairs and providing a certain lubricating effect. Consistent with this

interpretation, S5 and S10 exhibit lower friction levels in Fig. 7(a). Figs. 9(d1-f3) present the microtopography of worn surfaces for different samples under a load of 30 N. A transformation in wear mechanism with the increasing load is evident, which is closely correlated with the elastic-plastic state of the materials. In general, elastic contact tends to induce abrasive wear, whereas plastic contact is prone to cause adhesive wear [48]. As shown in Fig. 9(d1), much fine wear debris is distributed on the surface of S0, a typical characteristic of abrasive wear. However, the magnified images in Figs. 9(d2) and 9(d3), corresponding to the red box in Fig. 9(d1), reveal the coexistence of slight plastic deformation and brittle spallation. The former was caused by local contact stress exceeding the material's yield limit, while the latter might result from microfracture of the hard-brittle phases due to stress concentration. In other words, the applied load (30 N) in this case has reached a critical threshold, thereby initiating the transition from abrasive wear to adhesive wear. Fig. 9(e1) provides the morphology of worn surfaces for S5 tested under 30 N. As compared to S0, a relatively smooth and integrated worn surface is exhibited. Undoubtedly, the addition of Cu—which enhances ductility—is the key determining factor. Such a tribological surface can contribute to a stable friction stage [25, 30], while its formation and destruction generally occur in a dynamic equilibrium during sliding [49, 50]. Therefore, to clarify the subsequent destruction mechanism of this in-situ formed worn surface, further observations were primarily conducted in this study, as shown in Fig. 9(e2). From these observations, an obvious adhesive wear mode can be considerably identified, evidenced by the severe plastic deformation present on the

surface [40]. Additionally, the image also reveals some microcracks that are perpendicular to the sliding direction; these cracks were mainly induced by cyclic shear stress generated during reciprocating friction. As the friction continued, these fatigue-induced microcracks gradually propagated and led to final surface peeling off.

By contrast, Figs. 9(f1) and (f2) show the worn surface morphologies of S10 under 30 N. Less spallation and slight plastic flow are observed, similar to the features observed under 10 N. Moreover, the corresponding EDS results in Fig. 9(f3) indicate that a relatively uniform heterogeneous surface structure was formed. Overall, it can be inferred that the wear resistance gradually improves with the increasing Cu content. This improvement is closely associated with the friction-induced mechanochemical reactions during sliding, which promote surface structural optimization and a more stable interfacial contact state between the friction pairs.

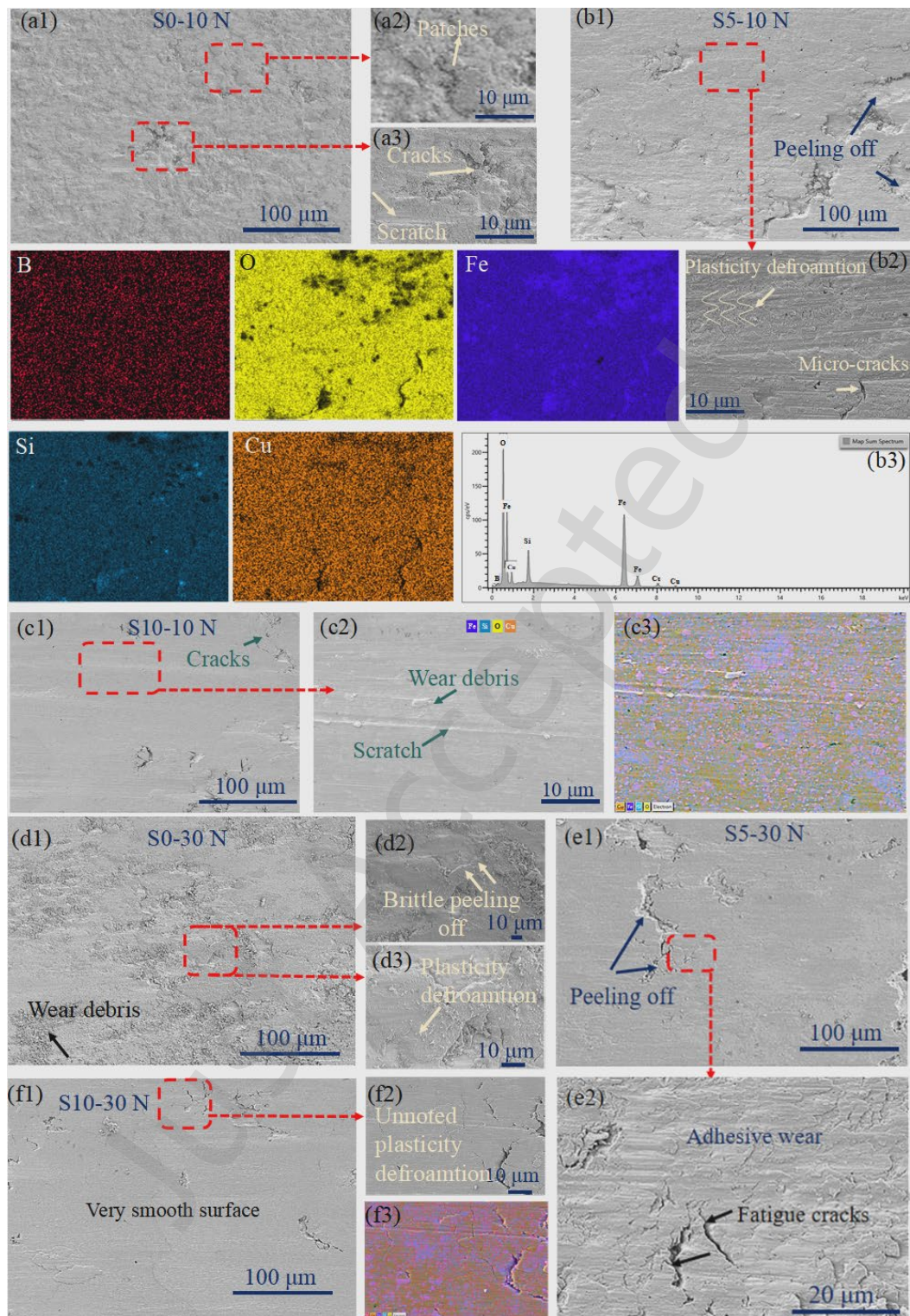


Fig. 9 Worn surface morphologies and corresponding EDS results of different samples under loads of 10 N and 30 N: (a1–a3) SEM images of the worn surface of S0 under 10 N; (b1–b3) SEM images and EDS results of S5 under 10 N; (c1–c3) SEM images and EDS results of S10 under 10 N; (d1) SEM image of the worn surface of S0 under 30 N, with (d2–d3) showing magnified views of the region marked in (d1); (e1) SEM image of the worn surface of S5 under 30 N, with (e2) showing the corresponding magnified view; (f1) SEM image of the worn surface of S10 under 30

N, with (f2) showing the corresponding magnified view and (f3) the elemental distribution of the region in (f2).

To verify this deduction, the finite element method (FEM) was applied to calculate the contact stress, as shown in Figs. 10(a-c). The hexahedral solid element (C3D8R) was used throughout the finite element model. To determine the mesh size satisfying the calculation accuracy, a mesh convergence analysis was performed in this study. By comprehensively balancing numerical precision and computational efficiency, a mesh size of 0.1 mm was finally determined. Two distinct normal loads of 10 N and 30 N were applied to the small ball, which slides on the S0 plate. The interfacial friction coefficient was defined based on the experimental measurement data. The bottom surface of the specimen was fully fixed and constrained. The sliding speed was 0.2 m/s.

When the load was 30 N, the maximum stress was about 1.7×10^3 MPa, exceeding the material's yield limit (1.451×10^3 MPa, as shown in Table 1); but when the load was 10 N, the maximum stress was about 5.2×10^2 MPa. It means that the higher load condition could result in plasticity deformation of material's interface during sliding, and thus, enhanced the tendency toward adhesive wear, which can be confirmed by the morphologies of worn surfaces in Fig.9(d1-d3). By contrast, the lower load with elastic deformation mainly caused abrasive wear, as shown in Fig. 9(a1-a3).

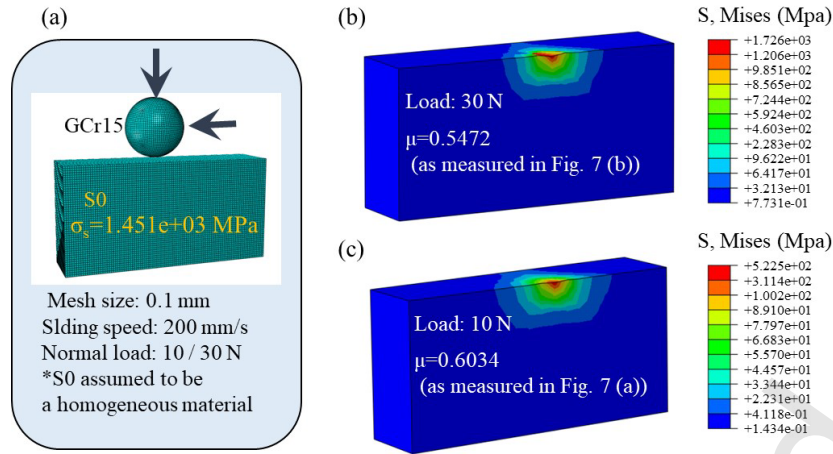


Fig. 10 FEM analysis of contact state under different loads: (a) boundary conditions and initial conditions, (b) the results for 30 N, (c) the results for 10 N.

3.5 Microstructure evolution

To elucidate the mechanochemical reactions during sliding and the corresponding wear-protection mechanisms, the cross-sectional microstructural evolution of the worn surfaces was investigated. Herein, the EBSD technology was used to characterize the cross-sectional microstructure of wear tracks. Fig. 11(a) reveals the inverse pole figure (IPF) of S0 after the wear test under 10 N. A notable phenomenon is observed wherein the crack propagation paths coincide with the regions where broken crystals are generated. Fig. 11(b) further illustrates the corresponding phase distribution. It is evident that the hard-brittle Fe_2B phase governed the initiation and propagation of cracks. The Kernel average misorientation (KAM) map in Fig. 11(c) indicates that the strain mainly exists in the subsurface with a depth of about 20 μm . The BCC α -Fe matrix in this region released most of the contact stress through plastic deformation, whereas the Fe_2B -rich regions exhibited much more limited deformation capability. Moreover, Figs.12(a-f) reveal the mechanisms of crack initiation, as well

as the refining mechanisms of α -Fe during sliding wear. Within the Fe_2B crystal, numerous deformation twins are observed (Figs. 12(a) and (b)), which could be explained by its BCT crystalline structure with fewer slip systems. As the strain increased, an intergranular fracture was responsible for the microcracks initiation, as shown in Fig. 12(d). However, within the α -Fe crystal, severe deformation could increase dislocation density drastically (Fig. 12(c)), forming dislocation cells or dislocation walls (Figs. 12(e) and (f)). With continued straining, cell boundaries evolved into high-angle grain boundaries, ultimately subdividing coarse grains into homogeneous ultrafine or nanoscale grains [15].

Figs. 11(d-f) present the cross-sectional microstructure of wear track for S10 after 10 N test. In contrast to S0, Cu addition makes a significant influence on the material's failure behavior and stress-strain response. For instance, a large number of extra twinning structures are observed within the Cu crystalline regions—this is a typical deformation mechanism that has been extensively reported in relevant studies [28, 41]. More importantly, the introduction of Cu altered the crack initiation and propagation processes. First, the cracks initiation was no longer solely determined by the hard-brittle Fe_2B , but was also strongly dependent on the distribution of Cu crystalline phase. As shown in Fig. 11(e), many microcracks but with much shorter length generate within the α -Fe matrix, which is different from S0. This was attributed to that the Cu crystalline phase performed a better deformation capacity through dislocation slipping and twinning. Second, the subsequent propagation of microcracks was inhibited by the bridging effect of the ductile Cu phase, as indicated in Fig. 11(e).

Consequently, the length of the microcracks in S10 is significantly shorter than that in S0. Meanwhile, Fig. 11(f) summarizes the corresponding KAM distribution. The main strain coincides well with the Cu phase, which confirms the aforementioned deduction. In addition, the KAM value distribution maps demonstrate that the strain distribution in S10 extends to a greater depth of about 120 μm , while the strain magnitude is slightly reduced. This was ascribed to the discontinuous stress-strain transmission of Cu phase, which reduced the stress concentration at the subsurface.

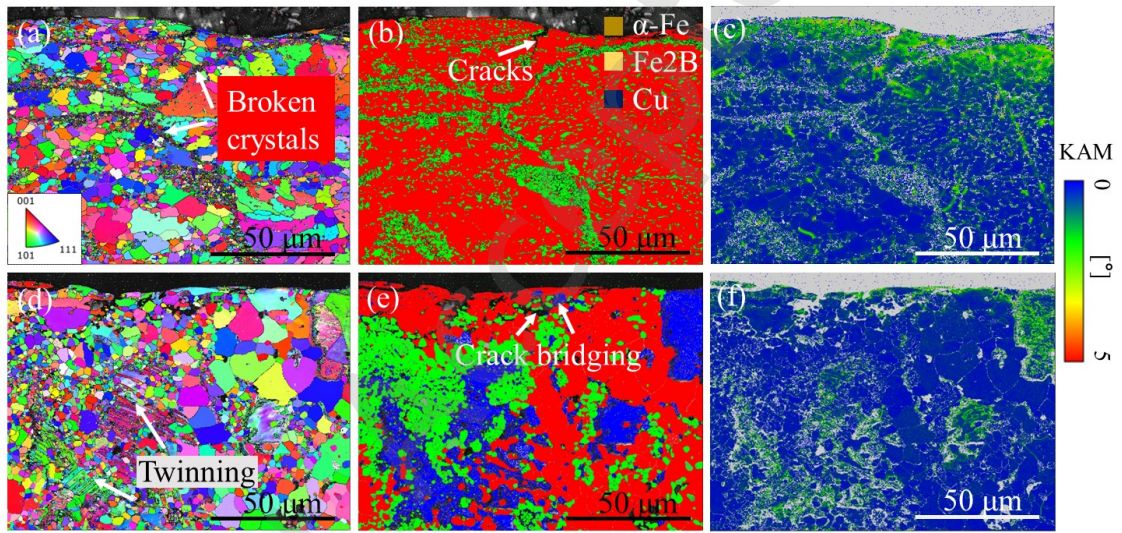


Fig. 11 Cross-sectional microstructure of wear tracks under 10 N: (a) the IPF of S0, (b) the phase distribution in S0, (c) the KAM map of S0; (d) the IPF of S10, (e) the phase distribution in S10, (f) the KAM map of S10.

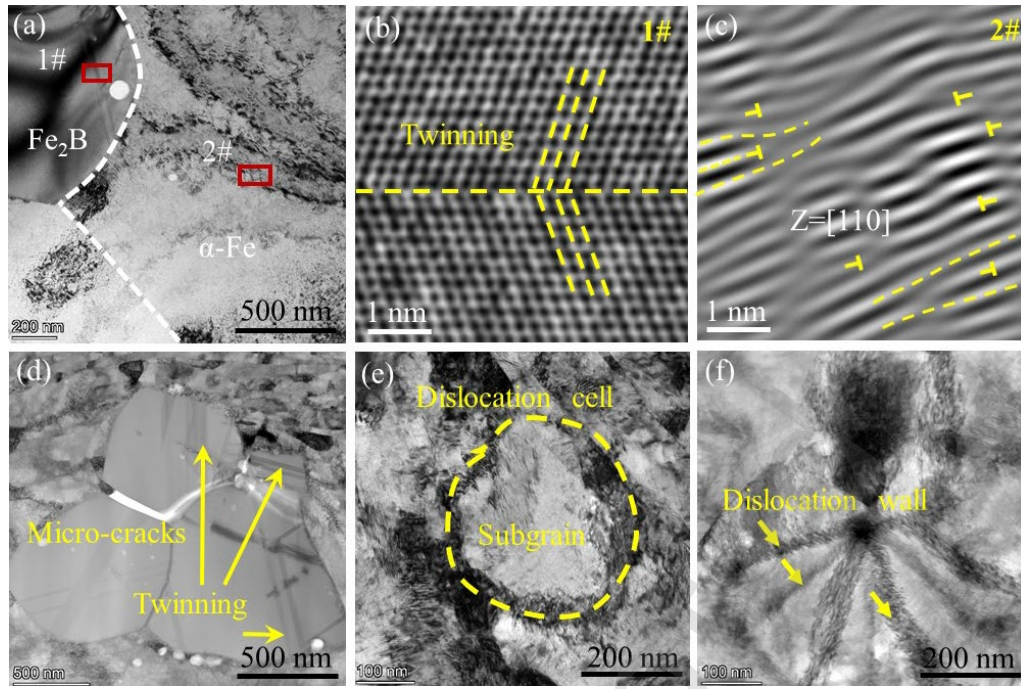


Fig. 12 Surface microcracks initiation mechanism for S0 under 10 N: (a) the bright field image of Fe_2B and $\alpha\text{-Fe}$; (b) the high-resolution image of Region 1# in (a); (c) the high-resolution image after Fourier transform for Region 2# in (a); (d) the microcracks initiation for Fe_2B phase; (e) and (f) the refining mechanism of $\alpha\text{-Fe}$.

Figs. 13(a-g) reveal the cross-sectional microstructures of wear tracks for S0 and S5 after tests under 30 N by using TEM technology. As shown in Fig.13(a), the bright field image of S0 indicates the formation of a tribological layer, which is not obvious when the load is 10 N (Fig. 11(a)). It suggests that the load condition played very important roles in mechanochemical reactions. Given that the formation and destruction of the layer occur simultaneously, a sufficiently high load is essential to maintain the layer's structural integrity and achieve dynamic equilibrium [38, 51]. Other relevant studies [52] have also proposed that elevated load input increases the interfacial temperature, thereby enhancing atomic activity. Fig. 13(b) provides the SAED patterns and high-resolution image of area 1#. It reveals that the tribological

layer is characterized by an amorphous structure. This was ascribed to the drastic friction-induced solid-state amorphization. Severe plastic deformation, frictional heating, and interfacial effects act synergistically to disrupt the long-range atomic order, thereby driving the atoms to form an amorphous structure characterized by short-range order yet long-range disorder [15, 16, 20]. To some extent, this self-adaptive behavior can improve its wear resistance when undertaking severe conditions. However, some microcracks can be observed within the layer, as shown in Fig. 13(c). These microcracks were attributed to the intrinsic brittleness of amorphous structure, and contributed a lot to the material's abrasive wear. The bright field image in Fig. 13(d) provides the cross-sectional morphology of the wear scar for S5, where a gradient structure is obviously exhibited. This was due to the gradually decreasing contact stress versus depth [15, 47]. In contrast to the discontinuous tribological layer in S0 (Fig. 13(a)), this continuous gradient tribological layer in S5 could avoid interfacial stress concentration by eliminating mechanical property discontinuity, and consequently, enhancing the interfacial bonding [47, 51]. Regarding the top region of the tribological layer, its magnified bright field image in Fig. 13(e) and corresponding high-resolution image in Fig. 13(g) indicate that some nanocrystals are embedded into the amorphous matrix. According to the corresponding SAED patterns, these nanocrystals exhibit a complex composition, predominantly consisting of nano-Cu with a small amount of nanoscale oxides. As discussed above, the nano-Cu phase could cooperate well with the amorphous matrix during plastic deformation through twinning and dislocation slip, an effective way to improve the toughness of the

tribological layer [28]. By contrast, the toughening ability of the hard nanoscale oxide was relatively limited. For example, Fig. 13(f) and the corresponding EDS results (elements distribution) reveal that the iron oxide nanocrystals mainly rely on path deflection to accommodate the plastic flow of the Fe-Si-B-O amorphous matrix. However, this mechanism may promote crack initiation under severe stress-strain conditions.

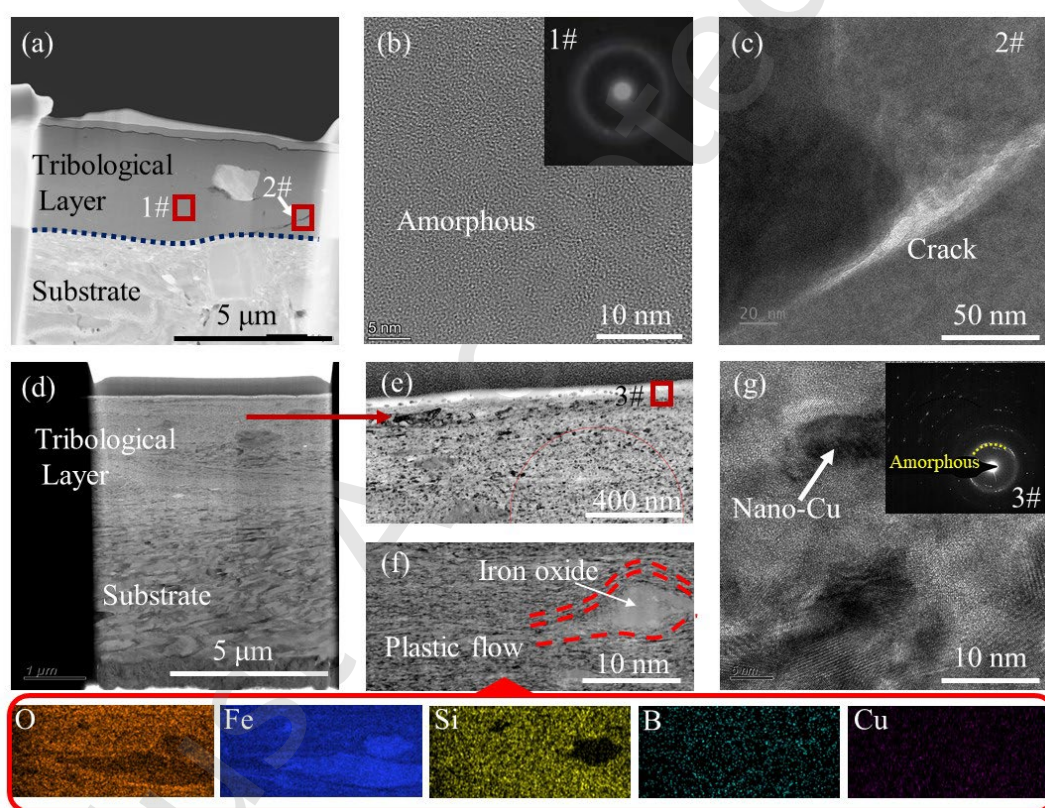


Fig. 13 Cross-sectional microstructure of wear tracks for S0 and S5 after tests under 30 N: (a) the bright field image of S0, (b) the high-resolution image marked by 1# in (a), (c) the high-resolution image marked by 2# in (a); (d) the bright field image of S5, (e) the magnified image from (d), (f) the roles of nanoscale oxide in plastic deformation, (g) the high-resolution image and SAED patterns marked by 3# in (e).

4 Conclusions

This study puts forward an innovative wear protection concept: in-situ constructing an amorphous-nanocrystalline composite tribological layer via friction-induced mechanico-chemical reactions. To realize this concept, an enthalpy-guided alloy design approach was primarily adopted to achieve thermodynamic advantages, while friction was supposed to provide the corresponding driving force. The conclusions are drawn as follows:

(1) The friction-induced structural evolution of the material surface exhibited a strong dependence on the applied load. Under a low-load condition (10 N), plastic deformation and grain refinement dominated the structural evolution. This was a purely physical process, and no mechano-chemical reactions took place. As the load increased to 30 N, an extra amorphous-nanocrystalline composite layer formed, consisting of nanocrystalline Cu embedded within the Fe-Si-B-O amorphous matrix. This demonstrated that friction-induced chemical changes occurred, namely the so-called mechano-chemical reactions.

(2) The wear performance was closely related to the structural features of the material surface. Compared with the predominantly amorphous tribological layer, the amorphous-nanocrystalline composite layer exhibited a better wear resistance. Under the severe 30 N condition, S10 maintained a low wear rate of $4.532 \times 10^{-5} \text{ mm}^3/(\text{N} \cdot \text{m})$, which was 27.43% lower than that of S0. This was because the nanocrystals improved the toughness of the amorphous matrix and reduced its tendency to crack originating from intrinsic brittleness under reciprocating contact conditions.

(3) The tribological contact inevitably introduced environmental oxygen into the alloy, which participated in the formation of the Fe-Si-B-O amorphous matrix. This was attributed to the emergence of new atomic coordination with considerable atomic-size mismatch, a well-known factor favorable for amorphous-phase formation. In addition, Cu exhibited a positive enthalpy of mixing with the main constituents of the alloy system. Its addition indeed produced the expected nanocrystals, which was critical for improving the wear resistance of the tribological layer.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

- [1] Liu C, Li Z, Lu W, et al. Reactive wear protection through strong and deformable oxide nanocomposite surfaces. *Nat Commun* **12**(1): 5518 (2021).

- [2] Zong H, Kang N, El Mansori M. Impact of applied loads on wear mechanisms in H13 steel at various preheating temperatures during laser powder bed fusion additive manufacturing. *Wear* 556–557: 205538 (2024).
- [3] Tang Y, Ji P, Li B, et al. Effect of loading on microstructure and friction and wear behavior of an austenite lightweight steel. *Tribol Int* 177: 108006 (2023).
- [4] Zhang B, Ma X, Liu L, et al. Sliding wear mechanisms and speed-load wear map of cylinder liner and piston ring under lubricated conditions. *Wear* 564–565: 205701 (2025).
- [5] Vencel A, Mrdak M, Hvizdos P. Tribological properties of WC-Co/NiCrBSi and Mo/NiCrBSi plasma spray coatings under boundary lubrication conditions. *Tribol Ind* **39**(2): 183–191 (2017).
- [6] Barman M, Barman T K, Sahoo P. Trends in corrosion resistance of electroless Ni-B-Mo coatings. *Tribol Mater* **4**(1): 38-55 (2025).
- [7] Dimitrova V, Dimitrov V, Zdravcheva G. Anodic and chrome coatings for firearm barrels: Microstructural and phase analysis. *Tribol Mater* **5**(1): 22–30 (2026).
- [8] Vencel A, Gligorijević B, Katavić B, et al. Abrasive wear resistance of the iron- and WC-based hardfaced coatings evaluated with scratch test method. *Tribol Ind* **35**(2): 123–127 (2013).
- [9] Laera A M, Massaro M, Dimaio D, et al. Residual stress and tribological performance of ZrN coatings produced by reactive bipolar pulsed magnetron sputtering. *Materials* **14**(21): 6462 (2021).
- [10] Wang J, Kaban I, Levytskyi V, et al. Ultra-high strength Co-Ta-B bulk metallic glasses: Glass formation, thermal stability and crystallization. *J Alloys Compd* 860: 158398 (2021).
- [11] Yuan J, Jing Z, Zhang Z, et al. Tribocorrosion behavior of Al-based amorphous coatings prepared by different spraying methods. *J Mater Res Technol* 35: 220–234 (2025).
- [12] Kumar A, Nayak S K, Bijalwan P, et al. Optimization of mechanical and corrosion properties of plasma sprayed low-chromium containing Fe-based amorphous/nanocrystalline composite coating. *Surf Coat Technol* 370:

255–268 (2019).

[13] Zhou Z, Zhang Z, Chen Y, et al. Composition optimization of Al-Ni-Ti alloys based on glass-forming ability and preparation of amorphous coating with good wear resistance by plasma spray. *Surf Coat Technol* 408: 126800 (2021).

[14] Si C, Duan B, Zhang Q, et al. Microstructure, corrosion-resistance, and wear-resistance properties of subsonic flame sprayed amorphous Fe-Mo-Cr-Co coating with extremely high amorphous rate. *J Mater Res Technol* 9(3): 3292–3303 (2020).

[15] Li B Y, Li A C, Zhao S, et al. Amorphization by mechanical deformation. *Mater Sci Eng R Rep* 149: 100673 (2022).

[16] Yin C, Liang Y, Liang Y, et al. Formation of a self-lubricating layer by oxidation and solid-state amorphization of nano-lamellar microstructures during dry sliding wear tests. *Acta Mater* 166: 208–220 (2019).

[17] Gosvami N N, Bares J A, Mangolini F, et al. Mechanisms of antiwear tribofilm growth revealed in situ by single-asperity sliding contacts. *Science* 348(6230): 102–106 (2015).

[18] Kumar B V M, Basu B, Vizintin J, et al. Tribochemistry in sliding wear of TiCN-Ni-based cermets. *J Mater Res* 23(5): 1214–1227 (2008).

[19] Assenova E, Vencel A. Tribology and self-organization in reducing friction: A brief review. *Tribol Mater* 1(1): 35–41 (2022).

[20] Ren Y, Huang Z, Wang Y, et al. Friction-induced rapid amorphization in a wear-resistant (CoCrNi)₈₈Mo₁₂ dual-phase medium-entropy alloy at cryogenic temperature. *Compos Part B Eng* 263: 110833 (2023).

[21] Okubo H, Nakae R, Iba D, et al. Tribological properties of 100% cellulose nanofiber (CNF) molding under dry- and boundary lubrication-conditions at CNF/steel contacts. *Cellulose* 30(11): 6887–6905 (2023).

[22] Yang L, Cheng Z, Zhu W, et al. Significant reduction in friction and wear of a high-entropy alloy via the

formation of self-organized nanolayered structure. *J Mater Sci Technol* 73: 1–8 (2021).

[23] Chu Z, Zhou Y, Xu F, et al. Study of friction and wear behaviors of Fe-based amorphous coatings by MD simulations. *Front Mater* 9: 1048443 (2022).

[24] Xie L, Wang Y. High temperature wear and corrosion behavior of detonation sprayed Fe-based amorphous coatings. *Sci Rep* 14(1): 29410 (2024).

[25] Gao X, Lin X, Yan Q, et al. Effect of Cu content on microstructure and mechanical properties of in-situ β phases reinforced Ti/Zr-based bulk metallic glass matrix composite by selective laser melting (SLM). *J Mater Sci Technol* 67: 174-185 (2021).

[26] Chong K, Gao Y, Zhang Z, et al. Glass forming ability and thermal stability of $(\text{ZrTiHfNi})_{100-x}\text{Nb}_x$ high entropy amorphous alloy. *J Mater Res Technol* 36: 699–712 (2025).

[27] Verma J, Pranav S, Jain A, et al. Exploring the role of thermodynamic parameters in determining Zr-Cu-Al-Ag glass-forming composition. *Metall Mater Trans A* 55(5): 1363–1376 (2024).

[28] Wu S H, Xue H, Yang C, et al. Hierarchical structure in Al-Cu alloys to promote strength/ductility synergy. *Scripta Mater* 202: 113996 (2021).

[29] Erutin D, Popovich A, Sufiiarov V. Selective laser melting of (Fe-Si-B)/Cu composite: Structure and magnetic properties study. *Metals* 13(2): 428 (2023).

[30] Li Y, Jia X, Xu Y, et al. Soft magnetic Fe-Si-B-Cu nanocrystalline alloys with high Cu concentrations. *J Alloys Compd* 722: 859–863 (2017).

[31] Larimian T, Chaudhary V, Christudasjustus J, et al. Bulk-nano spark plasma sintered Fe-Si-B-Cu-Nb based magnetic alloys. *Intermetallics* 124: 106869 (2020).

[32] Zhang Y. Alloying effects on nanostructure formation in iron based soft magnetic materials. Ph.D. Thesis. Singapore: Nanyang Technological University, 2007.

- [33] Kim J K, Shadangi Y, Min H G, et al. Alloy design strategies for Fe-rich particle manipulation via unveiling the solidification behavior of Cu-Fe-Si alloys. *Mater Des* 256: 114296 (2025).
- [34] Takeuchi A, Inoue A. Classification of bulk metallic glasses by atomic size difference, heat of mixing and period of constituent elements and its application to characterization of the main alloying element. *Mater Trans* 46(12): 2817–2829 (2005).
- [35] Zambrano O A, Iglesias-Guerrero B, Rodríguez S A, et al. Running-in period during sliding wear of austenitic steels. *Tribol Lett* 72(3): 70 (2024).
- [36] Sun W, Huang X, Zhang J, et al. The roles of microstructural anisotropy in tribo-corrosion performance of one certain laser cladding Fe-based alloy. *Friction* 11(9): 1673–1689 (2023).
- [37] Zheng K, Gao C, He F, et al. The role of rare earth lanthanum oxide in polymeric matrix brake composites to replace copper. *Polymers* 10(9): 1027 (2018).
- [38] Lin H Y, Cheng H Z, Lee K J, et al. Effect of carbonaceous components on tribological properties of copper-free NAO friction material. *Materials* 13(5): 1163 (2020).
- [39] Lan L, Wang W, Cui Z, et al. Mechanical, materials, and physicochemical effects on the high-temperature tribological behaviour of laser additive manufacturing AlCoCrFeNi_{2.1} eutectic high-entropy alloys. *Virtual Phys Prototyping* 19(1): e2355640 (2024).
- [40] Liu X, Gao J, Zhang Y, et al. Achieving optimized tribocorrosion resistance on Ti₅₁Zr₁₅Nb₁₄Mo₁₇Cu₃ alloy via precipitate engineering. *Corros Sci* 256: 113257 (2025).
- [41] Wang S, Ma Z, Liao Z, Song J, Yang K, Liu W. Study on improved tribological properties by alloying copper to CP-Ti and Ti – 6Al – 4V alloy. *Mater Sci Eng C* 57: 123-132 (2015).
- [42] Goudar D M, Haider J, Raju K, et al. Influence of Cu addition on the wear behavior of a eutectic Al-12.6Si alloy developed by the spray forming method. *J Compos Sci* 8(3): 88 (2024).

- [43] Zhu Z X, Liu X B, Liu Y F, et al. Effects of Cu/Si on the microstructure and tribological properties of FeCoCrNi high entropy alloy coating by laser cladding. *Wear* 512–513: 204533 (2023).
- [44] Chen C, Araby S, Demiral M, et al. Fatigue behavior and tribological properties of laser additive manufactured aluminum alloy/boron nitride nanosheet nanocomposites. *J Mater Res Technol* 20: 3930–3948 (2022).
- [45] Hong W, Cai W, Wang S, et al. Mechanical wear debris feature, detection, and diagnosis: A review. *Chin J Aeronaut* 31(5): 867–882 (2018).
- [46] Ho S C, Lin J H C, Ju C P. Effect of fiber addition on mechanical and tribological properties of a copper/phenolic-based friction material. *Wear* 258(5-6): 861–869 (2005).
- [47] Saffar A, Shojaei A. Effect of rubber component on the performance of brake friction materials. *Wear* 274–275: 286-297 (2012).
- [48] Guo Z, Lu X, Peng G, et al. Beyond first-cycle damage: Mechanistic drivers of fatigue crack nucleation in single crystals. *J Mech Phys Solids* 206: 106393 (2026).
- [49] He T, Zhu M, Li H, et al. Evolution of tribolayer in GH2132/GH4169 fretting wear at elevated temperatures. *Tribol Int* 214: 111225 (2026).
- [50] Zhang Y, Liang F, Lin Y, et al. Mitigating friction and wear by pre-designed or tribo-induced heterostructures: An overview. *Mater Res Lett* 12(8): 535–550 (2024).
- [51] Li S, Liu J, Wang Z L, et al. Mechano-driven chemical reactions. *Green Energy Environ* 10(5): 937–966 (2025).
- [52] Hu W, Wen B, Huang Q, et al. Role of plastic deformation in tailoring ultrafine microstructure in nanotwinned diamond for enhanced hardness. *Sci China Mater* 60(2): 178–185 (2017).