Synergistic lubrication of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction as a lubricant additive

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Received: 19 July 2021 / Revised: 31 August 2021 / Accepted: 02 November 2021

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Abstract: The few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterostructure was successfully prepared via vertically growing of MoS$_2$ nanosheets on the few-layer Ti$_3$C$_2$T$_x$ matrix using hydrothermal method. The tribological properties as additive in mineral oil (150N) were evaluated in detail. The 0.3 wt% of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterostructure addition amount can reduce the friction and wear of 150N by 39% and 85%, respectively. Moreover, the enhancement effect of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ on tribological properties of 150N is superior to that of few-layer Ti$_3$C$_2$T$_x$, MoS$_2$ nanosheets, and their mechanical mixture. Based on the characterization and analysis of wear debris and wear track, such excellent tribological properties of the few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterostructure derive from its structural advantage toward good dispersion, the synergistic lubrication of Ti$_3$C$_2$T$_x$ and MoS$_2$ nanosheets during the rubbing process, and the formation of tribo-film.

Keywords: few-layer Ti$_3$C$_2$T$_x$; molybdenum disulfide (MoS$_2$); heterojunction; tribological performance

1 Introduction

In the wake of the development of mechanical equipment, friction and wear of moving elements cause serious energy consumption and material losses. Therefore, reducing friction and wear is still currently a top priority [1–4]. Use of lubricating oil is one of the effective ways for friction reduction and wear resistance. Unfortunately, traditional lubricating oil can no longer meet the ever-increasing performance requirements under extremely working conditions. Recently, a series of functional additives have been developed to improve lubrication performance, like nanomaterials [5, 6], ionic liquids [7, 8], and polymers [9], etc. In terms of these functional additives, the two-dimensional (2D) nanomaterials have been broadly introduced into lubricants [10–13], like graphene, molybdenum disulfide (MoS$_2$), boron nitride, and so on.

MXene, as a novel 2D material, has received considerable attention since the first discovered by Drexel University scientists in 2011 [14]. MXenes are prepared by selected etching the “A” layer from layered ternary compound M$_n$+1AX$_n$ phases, where “M” is an early transition metal (e.g., Ti, Nb, Mo, Cr, and so on), “A” represents a group IIIA or IVA element, and “X” is C and/or N. Ti$_3$C$_2$T$_x$, as a kind of typical MXene material, has been extensively investigated for sensors, catalysts, lithium ion batteries, electrochemical capacitors, and other fields due to the rich chemistries and unique morphologies [15–21]. In addition, because of its outstanding mechanical strength, layered graphene-like structure, and low shear strength, Ti$_3$C$_2$T$_x$ is a highly potential additive to improve the lubrication properties. Zhang et al. [22] early investigated the tribological performance of Ti$_3$C$_2$T$_x$ as lubricant additive,
and proved that Ti$_3$C$_2$T$_x$ at the optimal concentration could positively improve the friction reduction and anti-wear due to the easily-shearing Ti$_3$C$_2$T$_x$ nanosheets and tribofilm on the sliding interfaces. Liu et al. [23] reported the effect of exfoliation degree on tribological properties of multilayer Ti$_3$C$_2$T$_x$ as a lubricating additive. The results proved that Ti$_3$C$_2$T$_x$ with a high exfoliation degree has excellent friction-reducing and anti-wear abilities. Nguyen et al. [24] reported that multilayer Ti$_3$C$_2$T$_x$ sheets as additives in water-based lubrication, exhibit remarkable enhancement in anti-friction and wear-resistant abilities. The above researches showed that even a small amount of Ti$_3$C$_2$T$_x$ could significantly improve the tribological performance of the fluid. Zhao et al. [25] measured the lubrication performance of graphene additives with different layer numbers, and few-layer graphene has better lubrication properties than multilayer graphene, as few-layer graphene can form an ordered tribofilm which parallels to the sliding direction at friction interface. Therefore, few-layer Ti$_3$C$_2$T$_x$ similar to few-layer graphene may also show good lubrication performance. However, when few-layer Ti$_3$C$_2$T$_x$ nanosheets were applied as lubricant additive, they tend to agglomerate because of their plentiful polar groups and high specific surface energy [26]. Therefore, a feasible way on overcoming the compatibility of nano-additives in oil is to synthesize the Ti$_3$C$_2$T$_x$-based nanocomposite with unique structure for inhibiting agglomeration.

In previous researches, MoS$_2$ has been demonstrated outstanding friction-reducing and anti-wear abilities as a lubricant additive due to the feeble van der Waals force between the interlayers and the strong covalent bonding within the intramolecular [27–29]. Chouhan et al. [30] reported that the reduced graphene oxide/MoS$_2$ heterostructure as an oil additive displays excellent synergistic lubricating behaviors. Interestingly, with the introduction of curved MoS$_2$ structure, the reduced graphene oxide/MoS$_2$ heterostructure is easier for dispersion in base oil [30–32]. In addition, small size MoS$_2$ nanosheets can be uniformly grown on few-layer Ti$_3$C$_2$T$_x$ matrix. So MoS$_2$ is a good candidate for preparing Ti$_3$C$_2$T$_x$-based nanocomposite to improve the tribological properties of few-layer Ti$_3$C$_2$T$_x$.

In this study, few-layer Ti$_3$C$_2$T$_x$ was prepared by the adjusted minimally intensive layer delamination method [33]. Then, few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction was synthesized by hydrothermal method. The tribological performance of Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction in mineral oil (150N) was tested by a UMT-3 tribotester, and its lubricant mechanism was further investigated. By comparing the lubrication properties of Ti$_3$C$_2$T$_x$, MoS$_2$, and their mechanical mixture, the synergistic effect of heterojunction was explored, and a probable lubrication mechanism was proposed according to the results.

2 Experimental details

2.1 Materials

Ti$_3$AlC$_2$ powder was provided by Ningbo Beijiaer New Material Co., Ltd., China. (NH$_4$)$_6$Mo$_7$O$_24$·4H$_2$O, HCl, LiF, thiourea, absolute ethyl alcohol, acetone, and other chemical reagents were purchased from Chengdu Kelong Chemical, China. All chemical reagents were directly used without further purification. Deionized water was synthesized in the laboratory.

2.2 Preparation of few-layer Ti$_3$C$_2$T$_x$

The synthesis of few-layer Ti$_3$C$_2$T$_x$ draws lessons from the minimally intensive layer delamination synthesis method. First, 20 mL 9M HCl and 1.6 g LiF were added to the PTFE reactor, and the mixture was continually stirred at room temperature until LiF particles were fully dissolved to form an etchant. Then, 1 g Ti$_3$AlC$_2$ was carefully and slowly added to the above etchant within 5 min to dissipate initial overheating caused by exothermic nature of the reaction. After that, the obtained suspension was continuously stirred at 35 °C for 24 h. Subsequently, the resulting acidic suspension was repeatedly centrifuged and washed with deionized water until the suspension reached a pH of about 7. The black sediment at the bottom of the centrifuge tube, containing Ti$_3$C$_2$T$_x$ and non-etched Ti$_3$AlC$_2$, was collected and cautiously moved into a 300 mL beaker containing 150 mL deionized water. The dispersion was treated by ultrasonication in ice water under a N$_2$ atmosphere for 30 min. Finally, the dispersion after ultrasonication was centrifuged at 5,000 rpm for 10 min, and the
supernatant containing few-layer Ti$_3$C$_2$T$_x$ was carefully obtained and dried.

2.3 Preparation of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction

Few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction was synthesized by hydrothermal method. Firstly, 0.7062 g (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and 1.5224 g thiourea were gradually submerged in 20 mL of deionized water by ultrasound for 30 min to get a homogeneous solution. Then, 0.1173 g few-layer Ti$_3$C$_2$T$_x$ powder was dissolved in the solution by ultrasound for 30 min. The mixture was carefully transferred to a 50 mL Teflon-lined stainless-steel autoclave and hydrothermally treated at 210 °C for 18 h in the drying oven. After the reaction, the resultant product was repeatedly centrifuged, washed, and dried to obtain few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction.

2.4 Characterizations

X-ray diffraction (XRD, Rigaku Smartlab, Japan) patterns were performed to characterize crystallinity and phase structure of samples with Cu K$_\alpha$ radiation ($U = 40$ kV, $I = 40$ mA, and $\lambda = 0.154$ nm). The microstructure and morphology of samples were characterized using a field-emission scanning electron microscopy (SEM, FEI Inspect F50, USA). Raman spectra (DXR, Thermo Fisher, USA) was excited with a 532 nm excitation laser and X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, USA) were performed to observe chemical composition and chemical state of samples. Atomic force microscope (AFM, FM-Nanoview1000AFM, China) was measured to characterize the height profiles of the few-layer Ti$_3$C$_2$T$_x$.

2.5 Friction and wear performances

In the friction tests, mineral oil (150N) was selected as base oil. The prepared additives were dispersed into the 150N by stirring and ultrasonic treatment for 5 min. The tribological behaviors of samples were evaluated using the ball-on-plate friction tests on the multi-function reciprocating sliding tribometer (CETR UMT-3, USA) under the condition of drying in air. In addition, the counterpart ball and lower steel substrates were GCr15 bearing steel with the hardness of 710 HV and the surface roughness of Ra = 50 nm. The counterpart balls were cleaned by an ultrasonic bath in acetone before testing. And the sliding amplitude, oscillation frequency, and duration of every experiment were 1 mm, 5 Hz, and 60 min, respectively. White light interferometer (Bruker Contour GT, Germany) was used to obtain the wear volume of wear track. The chemical state and morphologies of the friction surface were characterized by X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, USA) and field-emission scanning electron microscopy (SEM, FEI Inspect F50, USA). To further explore the nanostructure transformation of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction after friction tests, the wear debris was carefully collected and cleaned for analysis.

3 Results and discussion

3.1 Chemical and structural characterization of nanomaterials

The synthesis process of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction is depicted in Fig. 1. First, Ti$_3$AlC$_2$ powders were etched in an etchant composed of LiF salts and HCl solution to get multilayer Ti$_3$C$_2$T$_x$. Then, few-layer Ti$_3$C$_2$T$_x$ was obtained with the assistance of appropriate ultrasonication. Finally, the few-layer Ti$_3$C$_2$T$_x$ was dispersed in a clear solution containing (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and thiourea to synthesize few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction using hydrothermal method. During the hydrothermal preparation process, the oxygen-containing functional groups on the surface of few-layer Ti$_3$C$_2$T$_x$ can be used as sites for the growth of MoS$_2$, and the MoS$_2$ nanosheets are vertically and uniformly grown on the surface of few-layer Ti$_3$C$_2$T$_x$ [34].

SEM images of multilayer Ti$_3$C$_2$T$_x$, MoS$_2$, few-layer Ti$_3$C$_2$T$_x$, and few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterostructure are shown in Figs. S1 and S2 in the Electronic Supplementary Material (ESM) and Figs. 2(a)–2(c). The pure MoS$_2$ sample (Fig. S1 in the ESM) is composed of MoS$_2$ nanosheets, which aggregates into a spherical shape due to the lack of Ti$_3$C$_2$T$_x$ as a matrix. After LiF and HCl etching Al layers, the Ti$_3$AlC$_2$ with bulk structure is successfully transformed into a typical organ-like Ti$_3$C$_2$T$_x$ structure, which indicates the successful removal of the Al atomic layer (Fig. S2 in
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Fig. 2  SEM images of (a) few-layer Ti$_3$C$_2$T$_x$ and (b, c) few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterostructure. (d) Elemental mapping images of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterostructure.

Fig. 1  Schematic illustration on synthesis of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction.

Friction (12): 2018–2032 (2022)

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It is obvious that the few-layer Ti$_3$C$_2$T$_x$ (Fig. 2(a)) is successfully obtained by the ultrasonication of multilayer Ti$_3$C$_2$T$_x$ dispersion, and the number of layers is significantly reduced. Compared with multilayer Ti$_3$C$_2$T$_x$, the few-layer Ti$_3$C$_2$T$_x$ has a larger specific surface area, which can provide more matrices for the growth of MoS$_2$ nanosheets to alleviate the agglomeration of MoS$_2$ nanosheets. After the hydrothermal reaction, MoS$_2$ nanosheets are vertically and uniformly grown on the few-layer Ti$_3$C$_2$T$_x$ matrix to synthesize few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterostructure (Figs. 2(b) and 2(c)). The in situ generated MoS$_2$ is tightly bound to the few-layer Ti$_3$C$_2$T$_x$, which reduces the agglomeration of MoS$_2$ nanosheets and expands the few-layer Ti$_3$C$_2$T$_x$ layer spacing. As shown in Fig. 2(d), elemental mapping images further show the uniform distribution of Mo, S, Ti, and C in entire the few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterostructure, suggesting that MoS$_2$ was uniformly attached on the few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterostructure surface in the form of nanosheets.

In order to further prove that the prepared Ti$_3$C$_2$T$_x$ is few-layer Ti$_3$C$_2$T$_x$, the thickness of the Ti$_3$C$_2$T$_x$ is investigated by atomic force microscopy (AFM). AFM height profile in Fig. 3 shows the Ti$_3$C$_2$T$_x$ with a thickness of about 4.7 nm. It is well known that the thickness of a monolayer Ti$_3$C$_2$T$_x$ is 0.98 nm, and the adsorbed water also contributes to the thickness [35–37]. Therefore, the 4.7-nm-thick flake should be three layers structures, which indicates that few-layer Ti$_3$C$_2$T$_x$ has been successfully prepared.

The crystalline structures, chemical composition,
and chemical state of the samples were investigated using XRD, Raman spectra, and XPS in Fig. 4. Figure 4(a) shows the characteristic peaks in the XRD patterns of few-layer Ti3C2Tx, MoS2, and few-layer Ti3C2T/MoS2 heterostructure. The diffraction peaks at 2θ of 9.4°, 32.3°, and 57.8° correspond to the (002), (100), and (110) planes of MoS2, respectively, demonstrating the formation of a layered structure of MoS2 [38]. After etching and delamination, the characteristic peaks at 6.7°, 34.5°, 38.9°, and 60.8° can be indexed to the (002), (0010), (0012), and (110) planes of few-layer Ti3C2Tx, respectively [39, 40]. The diffraction peaks of MoS2 can be clearly observed in the few-layer Ti3C2T/MoS2 heterostructure. However, the (002) plane of few-layer Ti3C2T does not appear in the heterojunction. Possible factors are that the intercalation of MoS2 and NH4+ during hydrothermal synthesis leads to a lower angle deviation of the (002), so no peaks are captured in 5°–80° [41]. The hydrothermal reaction causes the partial oxidation of Ti3C2T and the formation of TiO2, so the XRD peak located at 25.2° can be attributed to the (101) peak of TiO2 [42].

The Raman spectra of the few-layer Ti3C2Tx, MoS2, and few-layer Ti3C2T/MoS2 heterostructure are shown in Fig. 4(b). The typical modes of few-layer Ti3C2Tx are clearly observed. The characteristic peaks appearing at 406 and 609 cm⁻¹ can be indexed to the Ti3C2Tx, indicating the successful preparation of few-layer Ti3C2Tx [43]. The prepared MoS2 and few-layer Ti3C2T/MoS2 heterostructure show two strong characteristic peaks at 371 and 397 cm⁻¹, which can be indexed to typical E1g and A1g peaks of MoS2, suggesting that the pure MoS2 and few-layer Ti3C2T/MoS2 heterostructure were successfully produced by hydrothermal route [44]. As the laser cannot penetrate through the MoS2 nanosheets on the surface of Ti3C2T nanosheets, so showing no characteristic peaks of underlying Ti3C2T nanosheets in the few-layer Ti3C2T/MoS2 heterojunction. Therefore, the Raman spectra of MoS2 and few-layer Ti3C2T/MoS2 heterojunction are familiar.

The XPS analysis of few-layer Ti3C2T/MoS2 heterostructure is investigated and the test result is shown in Fig. 4(c). The full-scale XPS pattern of few-layer Ti3C2T/MoS2 heterostructure reveals that
Mo, S, Ti, C, and O are the predominant elements and no other impurity elements, which further manifests the high purity of the few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterostructure.

### 3.2 Tribological performance of lubricant additives

The friction coefficient and wear volume of dispersions of 150N with different concentrations of few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterojunction are shown in Fig. 5. The friction coefficient of pure 150N showed a gradual rise and then tended to considerably fluctuate around 0.14, which possibly emerged the direct contact on the wear surface under the boundary lubricating condition. However, using the few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterojunction as an additive greatly improved the tribological properties of the 150N. In the concentration range of 0.1–0.9 wt%, the friction coefficient and wear volume of 150N with additives are lower than those of pure 150N. In addition, with the adding of few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterojunction, the friction coefficient curve will eventually smooth and stabilize after the initially slight fluctuation, which is obviously different from the friction coefficient curve of 150N without additives. The above results show that the few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterojunction has a good tribological performance. As the increase of added concentration, the average friction coefficient first decreases and then increases. When the concentration is less than 0.3 wt%, the tribological performance is poor because the amount of nano additives is not enough to support the formation of a uniform and dense friction film between the pair of grinding pairs; When the concentration is greater than 0.3 wt%, the heterojunction is prone to agglomeration and cannot enter the friction interface, which leads to poor tribological performance. From the above experiment, the results show that few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterojunction has the first-class friction-reducing and anti-wear abilities at an addition amount of 0.3 wt%. So, subsequent experiments selected an additive concentration of 0.3 wt%.

To comprehensively evaluate the lubricating performance of few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterojunction under different loads, friction tests were also performed at 20, 60, 100, and 140 N in Fig. 6. The results showed that, compared to pure base oil without additives, the mean friction coefficient of the lubricants with heterojunction additives was reduced by 27.9%, 31.7%, 32.8%, and 38.9% under 20, 60, 100, and 140 N loads, respectively. Obviously, as the load increases, the effect of friction reduction gets better and better. The reason may be that it is easier to form a stable tribochemical film under the high loads. As can be seen from Fig. S3 in the ESM, compared with base oil, the lubricants with the heterojunction additives can make the friction curve more stable under different loads. The reason may be that the few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterojunction formed a stable tribofilm on the surface of counterpart. It is obvious that the few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterojunction improved the tribological performance of 150N at different loads, which should benefit from the good synergistic lubrication performance of few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterojunction.

In order to investigate the synergistic effect of few-layer Ti$_3$C$_2$Tx/MoS$_2$ heterojunction, the friction coefficient curves and wear volume of few-layer

![Fig. 5](image_url) (a) Friction coefficient curves and (b) wear volumes lubricated by 150N with few-layer Ti$_3$C$_2$Tx heterojunction additive at different concentrations.
Fig. 6 Variations of the mean friction coefficient and wear volumes lubricated by few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction with the increasing load.

Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction were compared with pure few-layer Ti$_3$C$_2$T$_x$, MoS$_2$, and their mechanical mixture (Fig. 7). Under the load of 140 N, the average friction coefficient of 150N, few-layer Ti$_3$C$_2$T$_x$, MoS$_2$, Ti$_3$C$_2$T$_x$/MoS$_2$ mixture, and few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction are 0.1332, 0.1222, 0.1093, 0.1438, and 0.0814, respectively. Figure 7 shows that except for mechanical mixture, all other additives in 150N can reduce the friction coefficient and wear volume. The friction coefficient and wear volume of pure few-layer Ti$_3$C$_2$T$_x$ are not significantly reduced, which may be caused by the fact that the load-bearing capacity of few-layer Ti$_3$C$_2$T$_x$ is not good and the few-layer Ti$_3$C$_2$T$_x$ is easier to agglomerate due to its plentiful polar groups and high specific surface energy [26, 45]. Compared with pure few-layer Ti$_3$C$_2$T$_x$, pure MoS$_2$ exhibits better performance. This is because MoS$_2$ is a recognized 2D layered lubricating additive, which can have better tribological properties under high loads, being consistent with previous studies [46, 47]. Apparently, the few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction additive exhibits the smallest wear volumes (decreased by 83.52%) and lowest friction coefficient (decreased by 38.85%). In addition, compared with unstable and fluctuate friction curve of other additives, the heterojunction has a more smooth and stable friction curve and lower average friction coefficients. Therefore, the few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction has superior tribological performance than individual few-layer Ti$_3$C$_2$T$_x$ or MoS$_2$, which benefits from the synergistic lubrication of few-layer Ti$_3$C$_2$T$_x$ and MoS$_2$ nanosheets in the heterojunction.

The three-dimensional (3D) morphologies, cross-sectional profile, and SEM images were investigated to intuitively observe the wear surface of the steel discs lubricated with pure 150N and 150N containing 0.3 wt% of the few-layer Ti$_3$C$_2$T$_x$, MoS$_2$, Ti$_3$C$_2$T$_x$/MoS$_2$ mixture, and few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction and the results are shown in Fig. 8. Obviously, the wear track lubricated with pure 150N is the deepest (Fig. 8(a)), and there are many furrows on the wear surface (Fig. 8(a)), demonstrating the serious adhesion wear. In addition, the wear tracks lubricated with Ti$_3$C$_2$T$_x$, MoS$_2$, and mechanical mixture describe slight abrasive wear. Compared with the Ti$_3$C$_2$T$_x$, MoS$_2$, and their mechanical mixture, the wear track lubricated with 150N containing few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction shows the shallowest and smoothest wear surface (Figs. 8(e)–8(e)), which also reflects the extremely excellent synergistic lubrication effect of Ti$_3$C$_2$T$_x$ and MoS$_2$ in the heterojunction.

Fig. 7 (a) Friction coefficient curves and (b) wear volumes lubricated by 150N with Ti$_3$C$_2$, MoS$_2$, Ti$_3$C$_2$/MoS$_2$ mixture, and few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction additive.
3.3 Analysis of friction mechanism

The wear situation of wear track under 150N with 0.3 wt% few-layer Ti₃C₂Tex/MoS₂ heterojunction lubrication were further checked by SEM with EDS to prove the existence of a uniform friction film. As shown in Fig. 9(b), Mo, S, Ti, and C are uniformly distributed on the surface of wear track. It is demonstrated for all the characterizations that the formation of deposited few-layer Ti₃C₂Tex/MoS₂ heterojunction on the rubbing surfaces exerts an enormous function on reducing friction and wear.

The formation of friction film benefits from good dispersion of additives in base oil. As shown in Fig. S4 in the ESM, only the few-layer Ti₃C₂Tex/MoS₂ heterojunction in base oil can remain dispersible stability after 4 d, while other additives have completely precipitated after 4 d. The vertically grown MoS₂ has a steric hindrance effect and inhibits the agglomeration of Ti₃C₂ nanosheets [48]. In the meantime, few-layer Ti₃C₂Tex nanosheets provide growth sites for MoS₂ to keep MoS₂ away from agglomerating into a spherical shape (Fig. 2(b) and Fig. S1 in the ESM).

The XPS spectrum of the worn surface lubricated with few-layer Ti₃C₂Tex/MoS₂ heterojunction was investigated to further make clear the lubrication...
mechanism. The full-scale XPS pattern from the binding energy of 0 to 800 eV and the fitted XPS fine spectra of Fe 2p, O 1s, Mo 3d, S 2p, and Ti 2p on the wear track are shown in Fig. 10. The full spectrum in Fig. 10(a) shows not only the predominant Fe and O elements, but also the presence of Mo, S, Ti, and C elements, which was consistent with the result of mapping in Fig. 9(b). As shown in Figs. 10(b) and 10(e), the FeO and FeO signals in Fe 2p and O 1s peaks indicate that some Fe elements have been oxidized during the friction process [49]. Furthermore, the FeSO4 signals in Fe 2p peak (Fig. 10(b)) and S 2p peak (Fig. 10(d)) illustrate that the Fe and S elements can have chemical reaction to form a new friction protection film [31, 50]. The XPS spectra of Mo 3d shown in Fig. 10(c) is composed of four peaks corresponding to MoS2 (230.1 and 233.6 eV) and MoO3 (234.5 and 236.8 eV), respectively [51]. Ti 2p peak (Fig. 10(f)) is composed of Ti–O bonding and Ti–C bonding [52]. Therefore, the above XPS analysis is inferred that the few-layer Ti3C2Tx/MoS2 heterojunction can be deposited on the rubbed surface and form an adsorption film. The adsorption film is mainly composed of MoS2 and few-layer Ti3C2Tx, which can be determined from the peaks of Mo 3d, S 2p, and Ti 2p. Then, due to the friction-heat and high pressure of the sliding surfaces, the part of adsorption film is converted into the tribofilms which are composed of MoO3, FeSO4, iron oxide, and compound containing the C–O bonding on the lubricated metal surface. The tribo-film is strongly adsorbed on the worn surface to protect the friction interface and plays an effective

![Fig. 9](image-url) (a) SEM and (b) mapping of the tribofilm lubricated with few-layer Ti3C2Tx/MoS2 heterojunction.

![Fig. 10](image-url) XPS spectra of (a) fully scanned spectra, (b) Fe 2p, (c) Mo 3d, (d) S 2p, (e) O 1s, and (f) Ti 2p on the surface of wear track lubricated with few-layer Ti3C2Tx/MoS2 heterojunction dispersed 150N.
role on reducing friction and wear.

In order to determine the structural transformation of additives, the SEM with EDS mapping analysis of the wear debris was observed in Fig. 11. EDS mapping shows that Mo, S, Ti, and C are uniformly distributed on the nanosheets of wear debris collected from the wear track, indicating that the wear debris is the few-layer Ti₃C₂Tₓ/MoS₂ heterojunction. Compared with the prepared few-layer Ti₃C₂Tₓ/MoS₂ heterojunction (Fig. 2(c)), the local regions of MoS₂ nanosheets on the surface of few-layer Ti₃C₂Tₓ/MoS₂ heterojunction evolved from a vertical to a parallel arrangement after friction. The change in this arrangement contributes to the exfoliation of the MoS₂ nanosheets from the few-layer Ti₃C₂Tₓ/MoS₂ heterojunction during the rubbing process, and leading to exfoliated small size MoS₂ nanosheets to penetrate into the pits and valleys of the reciprocating surfaces and reducing the direct contact with metal surfaces [53].

Here, the lubrication mechanisms of few-layer Ti₃C₂Tₓ/MoS₂ heterojunction as an additive in the 150N base oil can be described in Fig. 12. In the running-in phase of friction, owing to the good dispersion given by the steric hindrance effect of heterojunctions, the few-layer Ti₃C₂Tₓ/MoS₂ heterojunction in oil can be continuously entered and deposited in the contact area. Then, under pressure and shear action, the vertical arrangement of MoS₂ nanosheets is transformed into parallel arrangement, and separated from the Ti₃C₂Tₓ nanosheets. The separated small size MoS₂ nanosheets penetrate into the contact area and gradually deposit in the asperities of the reciprocating surfaces to form a more dense and uniform friction film. The larger Ti₃C₂Tₓ nanosheets can fill up the pits and valleys and make the contact surface smoother. In the process of friction, the applied load at rapid reciprocating movement produces high temperature and pressure, which leads to the damage of thin adsorption film. Under high temperature and pressure action, the deposited few-layer Ti₃C₂Tₓ/MoS₂ heterojunction will go through complicated tribochemical reactions, which forms a new chemical film.
transfer film and improves the interaction of friction-interfaces. In conclusion, the excellent lubrication performance of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction benefits from the synergistic lubrication effect.

4 Conclusions

The lubrication behavior of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction as oil additives was studied. The lubrication mechanism was investigated by analyzing the chemical nature, morphology of wear debris and wear track. The significant conclusions are elucidated as follows.

1) Few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction was prepared through hydrothermal method. MoS$_2$ nanosheets are vertically and uniformly grown on the surface of few-layer Ti$_3$C$_2$T$_x$ owing to the interaction between the oxygen-containing functional groups of the few-layer Ti$_3$C$_2$T$_x$ and Mo precursor.

2) The lubrication performances of few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction is superior to those of few-layer Ti$_3$C$_2$T$_x$, MoS$_2$, or their mixture. The introduction of 0.3 wt% few-layer Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction into 150N can reduce friction coefficient and wear volumes by 38.85% and 83.52%, respectively.

3) The unique heterojunction structure with good dispersion and the friction-induced evolution of Ti$_3$C$_2$T$_x$/MoS$_2$ heterojunction are beneficial to give full play of synergistic lubrication.

4) The Ti$_3$C$_2$T$_x$/MoS$_2$-deposited film and tribocochemical film composed of MoO$_3$, FeSO$_4$, iron oxide, and compound can enhance the interaction of sliding interfaces, thereby effectively reducing the friction and wear.

Acknowledgements

The authors gratefully acknowledge the financial support provided by National Natural Science Foundation of China (No. 52075458) and Sichuan Science and Technology Program (No. 2021JDRC0094). Meanwhile, the authors gratefully acknowledge Analytical and Testing Center of Southwest Jiaotong University for supporting the SEM measurements.

Electronic Supplementary Material: Supplementary material is available in the online version of this article at https://doi.org/10.1007/s40544-021-0568-3.

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