Preparation of TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites and their tribological properties as base oil lubricant additives

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TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites were successfully prepared by a facile liquid phase synthesis technology. The phase structure and morphology of as prepared samples were analyzed by means of X-ray diffraction and scanning electron microscopy. The results revealed that uniform TiO$_2$ particles were distributed within the surface and edge of Ti$_3$C$_2$T$_x$ nanosheets. Subsequently, the tribological properties of the TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposite as lubricant additive in base oil were evaluated with a UMT-2 ball-on-disc tribotester, and the morphologies of worn steel surfaces were investigated using a scanning electron microscope and non-contact optical profile testing instrument. The results of the friction tests showed that base oil with 1 wt% TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposite under optimal load had excellent friction reduction. The morphology of the worn surface analyzed by SEM and non-contact optical profile testing confirmed that the hybrid nanocomposites mended the scratched surface and formed a uniform tribofilm, thereby helping to improve the tribological properties of the base oil. Furthermore, this work shows the promising applications of TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites in the field of tribology.

1. Introduction

In recent decades, ternary nanolaminated hexagonal ceramics M$_{n+1}$AX$_n$, where M is an early transition metal, A is an A-group element (mostly IIIA and IVA), and X is C and/or N, n = 1, 2, 3,..., has attracted great attention owing to their interesting properties and prospective applications. As an important representative member of M$_{n+1}$AX$_n$, Ti$_3$AlC$_2$ has excellent ceramic and metallic properties, such as low coefficient of friction, excellent thermal and electrical conductivity, easy machinability, high elastic modulus, chemical stability, good thermal stability and oxidation resistance, and has drawn mounting attention from researchers.

The laminated structure of Ti$_3$AlC$_2$ is comprised by alternating stacking of hexagonal TiC layers and congested edge-sharing bidimensional Al atomic layers along the c-axis, in which the bonding between Ti and C is firmly covalent, but the metallic bonding between Ti and Al is comparatively weak and therefore more susceptible to chemical reaction.

Lately, Naguib et al. reported to fabricate two-dimensional Ti$_3$C$_2$(OH)$_2$ nanosheets by selectively etching the Al layers with hydrofluoric acid (HF), following a similar process, other MAX phases have also been successfully exfoliated into the two-dimensional transition metal nanocarborides and nanonitrides named Mxenes, and has been made mounting attention from researchers.

Over the past decades, TiO$_2$, as a typical member of inorganic transition metal dioxides, has aroused numerous studies due to its attractive functional properties and promising applications. Furthermore, various hybrid modifications including surface modification, coupling with porous materials, and carbon coating have been executed to TiO$_2$ nanostructures in order to improve the properties. At present, several attempts have been made in the synthesizes and properties of TiO$_2$ hybrid nanostructures. Soraya Hosseini et al. studied the mesoporous carbon and TiO$_2$ photoanodes synthesized by sol–gel spin coating onto a glassy substrate, and found that the enhanced humic acid removal of TiO$_2$/C/C/TiO$_2$ photoanodes was due to the highest photocurrent density generated. Hong Z et al. fabricated the TiO$_2$@C–rGO hybrid nanostructures through in situ growth of oriented self-assembly of TiO$_2$ mesocrystals on GO route, the hybrid nanostructures display a high reversible capacity, superior rate capability, and long term cycling stability, which is largely attributed to the strong architecture of well-dispersed carbon-coated mesoporous TiO$_2$ mesocrystals anchored on conductive graphene network. Wongaree M et al.

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prepared CNT/TiO2 nanofibers by spinning CNT/poly(vinyl pyrrolidone) (PVP) solution followed by the removal of PVP, the synergistic effects of the larger surface area and lower band gap energy of CNT/TiO2 nanofibers were presented as robust adsorption ability and greater visible light adsorption. Qian L et al.31 produced biomorphic charcoal/TiO2 composites from moso bamboo templates, the C/TiO2 composites were exhibited lower geometrical density, better thermostability, and favorable microwave absorptive properties. Naguib M32 and Gao33 et al. fabricated TiO2/C nanohybrids by mild oxidation of Ti3C2, the obtained samples were exhibited extremely high cycling rates when tested as anodes and good photocatalytic activity. However, TiO2/Ti3C2T_x hybrid nanostructures and their application in the tribological field have rarely been reported.

In this work we report a simple method to prepare TiO2/Ti3C2Tx via immersing Ti3C2Tx powders in distilled water assisted hydrothermal reaction. Moreover, the tribological properties of TiO2/Ti3C2Tx composites as additives in the base oil were also investigated. This study will be useful for Mxene practical application in the future.

2. Experimental

2.1 Synthesis of TiO2/Ti3C2Tx composites

To fabricate the Ti3AlC2 powders, commercially powders of Ti (99.0 wt% purity, 40 μm), Al (99.97 wt% purity, 75 μm), and graphite (99.85 wt% purity, <30 μm), Sn (~99.0 wt% purity, 40–75 μm) were mixed with the stoichiometric ratios of 3Ti/1Al/1.8C/0.2Sn, the specific preparing procedure was detailed in our previous study.4 Briefly, powders in the appropriate proportion were magnetic stirring in absolute alcohol at 70 °C. After being dried and sieved, the powders were cold-pressed at 30 Mpa and then heated at 1450 °C under Ar for 20 min in a tube furnace, then taken out after cooling down to room temperature. The obtained Ti3AlC2 was crushed and sieved through a 300 mesh sieve.

To exfoliate the Ti3AlC2 to Ti3C2Tx (Mxenes), 5 g Ti3AlC2 powders was immersed in a 40 wt% aqueous hydrofluoric acid solution, and magnetically stirring for 100 h at room temperature. Afterwards the etched powder mixtures were filtered and washed with ethanol and distilled water several times, and dried to obtain Ti3C2Tx powders.

TiO2/Ti3C2Tx hybrid nanostructures were synthesized using a hydrothermal process. The prepared Ti3C2Tx was added to distilled water and stirring evenly, then the solution was transferred to a Teflon-lined autoclave and placed in an electric oven heated at 200 °C for different time. After the hydrothermal process, the as-prepared product was washed with distilled water and ethanol for several times and then dried at 60 °C for 12 h. Finally, black powders were obtained.

2.2 Characterisation of samples

The X-ray diffraction (XRD) experiments on the TiO2/Ti3C2Tx were performed on a Bruker D8 advance diffractometer under CuKa radiation. The 2θ range used in the measurement was from 7 to 70°, data analysis with Jade software. The morphologies and structures were investigated using a JSM-7001F scanning electron microscope (SEM) and a BRUKER ContourGT non-contact 3D optical profile testing instrument.

3. Results and discussion

The XRD patterns of the initial 3Ti/1Al/1.8C/0.2Sn mixture after heated at 1450 °C for 20 min. (Fig. 1a) show that the synthesized
powders mainly contain Ti$_3$AlC$_2$ with small amounts of TiC as a secondary phase. The characteristic diffractions of Ti$_3$AlC$_2$ were detected around 9.5° and 39.0°, respectively, corresponding to the (002) and (104) planes, which are consistent with the previous literature and the data in the standard card (JCPDS: 52-0875) for Ti$_3$AlC$_2$. According to the calculation from the XRD pattern, the purity of the sample is upto 96.7 wt%.

The size and morphology of Ti$_3$AlC$_2$ sample were identified by SEM. Fig. 1b shows the SEM images of the as-prepared Ti$_3$AlC$_2$ sample. Fig. 1b reveals that the sample consists of a lot of densely aligned laminated-like structure and smooth surface. Further observation shows that the particles have melting imprint, indicating the formation of liquid phase at high temperature, the result indicating that high-yield and good morphology of Ti$_3$AlC$_2$ could be readily achieved through this approach.

Fig. 2 gives the XRD patterns of the exfoliated Ti$_3$C$_2$T$_x$ powders obtained by 40% HF treatment. After HF treatment, the labelled diffraction peaks in Fig. 3I can be indexed to those of the phase of Ti$_3$C$_2$T$_x$ and TiC, the peaks indexed to Ti$_3$AlC$_2$ have clearly vanished. The XRD patterns of product verify the formation of Ti$_3$C$_2$T$_x$ phase. The strong peaks were found around 9.0° and 18.2° corresponding to (002) and (004) of Ti$_3$C$_2$T$_x$, which shift to lower 2θ angles contrasting to the diffraction of Ti$_3$AlC$_2$, manifesting the expansion along c-axis. Owing to the weak metallic bonding between Ti and Al, the Al layer is exfoliated by selective etching off Ti$_3$AlC$_2$ SEM images (Fig. 2) show that the obtained samples are uniform separated layers with an average thickness of about 10 nm.

Fig. 3 gives the X-ray diffractograms of Ti$_3$C$_2$T$_x$ before and after hydrothermal treatment in distilled water at 200 °C. The XRD patterns of the products of Ti$_3$C$_2$T$_x$ after treatment at 200 °C for 12 h can be indexed for both TiO$_2$ and Ti$_3$C$_2$T$_x$, in addition, it also can be clearly seen that the intensity of TiO$_2$ peaks increased as the reaction time increasing, while the fraction of not oxidized Ti$_3$C$_2$T$_x$ was greatly reduced. This reveals the kinetics of the oxidation process as a carbide consuming mechanism.

Fig. 4 exhibits a typical SEM images for Ti$_3$C$_2$T$_x$ sample treated at 200 °C for 24 h. It can be seen from Fig. 4a that there are many uniform oxide particles distributing within the surface and edge of the thinner layers, while the original microstructure of Ti$_3$C$_2$T$_x$ is separately layered structure (Fig. 2). The magnified SEM image (Fig. 4b) further gives the details of hybrid nanocomposite. There are significant amounts of TiO$_2$ co-exist with Ti$_3$C$_2$T$_x$, the size of TiO$_2$ particles is about 100 nm.

In order to discuss the evolutions of the friction coefficients of TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites, the concentration of the nanocomposites in the lubricant was studied. Several concentrations in the range from 0.6 wt% to 5 wt% were chosen. And the tests were carried out with 20 N, 150 rpm, 600 s and the

![Fig. 2 A typical SEM morphology of the synthesized multilayers Ti$_3$C$_2$T$_x$.](image)

![Fig. 3 XRD patterns of Ti$_3$C$_2$T$_x$ before and after hydrothermal treatment at 200 °C for 12 h and 24 h.](image)
room temperature, respectively. The friction coefficients of the tests are offered in Fig. 5a. It can be seen that under base oil lubrication, the friction coefficient has a decreasing trend over 300 s, and then stabled with an average value of 0.103. The base oil with 0.6 wt% TiO2/Ti3C2Tx hybrid nanocomposites lubrication has the same trend with the base oil lubrication, maintained a friction coefficient of approximately 0.075 after 300 s sliding. The base oil with 1 wt% TiO2/Ti3C2Tx lubrication showed the lowest friction coefficient of 0.073 with a slight decreasing trend. This may be because, with the continuous sliding, more and more TiO2/Ti3C2Tx were adhered to the friction surfaces creating a tight layer between the two contact surfaces, leading to a reducing friction coefficient. However the friction coefficient of base oil with 3 wt% concentration became erratic and lied along sliding time after 150 s sliding. When the base oil formulated with 5 wt% TiO2/Ti3C2Tx, the friction coefficient rose observably over 0.16 and an increasing trend with sliding time.

When the concentration of TiO2/Ti3C2Tx hybrid nanocomposites is 1 wt%, the best antifriction performance is achieved. The remarkable tribological property may due to their TiO2 nanoparticles and thin laminated structure. Furthermore, the nanoparticles can readily enter into the boundary with base oil and form a uniform shielded film, so the behavior of friction coefficient is more steady than others, but too much higher concentration of the nanoparticles revealed vast agglomeration, could not enter the contact area easily, also could damage the consistency of the gluey system of the base oil. So, the optimum concentration of the TiO2/Ti3C2Tx hybrid nanocomposites as an additive in base oil is proposed to be 1 wt%.

Fig. 5b reveals the change of friction coefficient of 1 wt% TiO2/Ti3C2Tx hybrid nanocomposites as an additive of lubricant under different loads, respectively. It can be observed that there is a trend that the friction coefficient of nanocomposites decreases firstly and then increases as the load increases, also, the curves of 30 N and 50 N have higher undulation than the curves of 5 N and 20 N. We can get the ideal load for friction display at 20 N. Within the scope of certain pressure, TiO2/Ti3C2Tx hybrid nanocomposites is delaminated readily at the contact region and precipitate a tribofilm, which can reduce shearing stress and generate a low friction coefficient. When the applied load is 5 N, TiO2/Ti3C2Tx cannot be compacted on the
friction surface to repair grinding crack, so the protective film was not shaped. Otherwise, if the applied load is too high, the protective film at the region will be damaged, finally inducing high undulation and friction coefficient.

With the aim of studying the wear resistance performance of TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites as lubricant oil additives, the grinding cracks of plate after friction were examined by SEM and BRUKER ContourGT non-contact 3D optical profile testing apparatus.

SEM photographs of the worn scar lubricated by base oil with different concentrations of TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites under 20 N are given in Fig. 6 and 7a. Fig. 6a presents that the rubbed surface lubricated by the pure base oil is quite rough with lots of wide and deep furrows along the sliding direction because of contact fatigue. In Fig. 6b and 7a, the worn surface lubricated with base oil added 0.6 and 1.0 wt% TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites is smoother than that lubricated with pure base oil. The furrows are shallower and subtler on the worn surface of steel disc under the lubrication of base oil with 0.6 and 1.0 wt% TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites than that lubricated with pure base oil. The furrows are shallower and no distinct mechanical damage on the worn surface of steel disc, meanwhile, a thin tribofilm is shaped on the substrate. However, under the load 50 N, as shown in Fig. 7b, the worn surface proves clearly coarse and the plastic deformation is rigorous, which is consistent with the higher and labile friction coefficient, as shown in Fig. 5b.

Fig. 8 illustrates grinding crack of the base oil with 1 wt% TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites at 150 rpm for 600 s under the load of 20 N and 50 N. It can be distinctly observed that the grinding crack under 20 N is composed of glossy and shallow furrows along the sliding direction (Fig. 8a), and the grinding crack caused by under 50 N (Fig. 8b) is wider and distributed irregular pits. From the images we can see that the depth and width of the wear scar for 20 N are about 30 $\mu$m and 280 $\mu$m respectively, while those for 50 N are about 35 $\mu$m and 400 $\mu$m. This manifests that the base oil with TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites under 20 N shown better anti-wear ability than 50 N.
The tribological tests and morphology of the grinding crack results suggest that the 1 wt% TiO$_2$/Ti$_3$C$_2$T$_x$ nanocomposites with the optimal load (e.g., 20 N) aids to form continuous and uniform tribofilm on the rubbing surface leading to friction reduction.

The tribological mechanism between the rubbing surfaces in base oil with TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites is ironically presented in Fig. 9. It is believed that the suitable content of TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites under appropriate load could enter in the gap between the friction surfaces easily. During sliding, the desquamated TiO$_2$ particles can mending the scratched surface to decrease the contact of rough between the friction surfaces, meanwhile the exfoliated Ti$_3$C$_2$T$_x$ sheets adsorb onto the rubbing surface and form a tribofilm, which can decrease shearing stress and the direct contact of tribopair, this is the main mechanism for improving the tribological behavior of TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites.

4. Conclusion

In brief, TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites were prepared by a liquid-phase reaction route. At a lower concentration (1 wt%) with the optimal load (e.g., 20 N), TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites could effectively improve the tribological properties of base oil by synergistic effects of mending the scratched surface and formation of a uniform tribofilm on the surface, which prevent the direct contact between counterparts during the friction process. This study suggests TiO$_2$/Ti$_3$C$_2$T$_x$ hybrid nanocomposites exhibit a potential application as oil-based lubricant additives.

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