Microstructure and tribological property of a MXene derived from Ti$_3$AlC$_2$

Fuyan Liu$^1$, Fujie Liu$^1$, Rui Zhang$^{3,4}$, and Xinhong Chen$^5$

$^1$ School of Chemical Engineering and Materials, Changzhou Institute of Technology, Changzhou 213032, People’s Republic of China

$^2$ Zhenjiang College, Zhenjiang 212028, People’s Republic of China

$^3$ School of Mechanical Engineering, Chengdu University, Chengdu 610106, People’s Republic of China

$^4$ Sichuan Province Engineering Technology Research Center of Powder Metallurgy; Chengdu University, Chengdu 610106, People’s Republic of China

$^5$ Jiangsu Alpha Purification Equipment Manufacturing Co., LTD, Taizhou 214500, People’s Republic of China

$^*$ Author to whom any correspondence should be addressed.

E-mail: liufy@czu.cn, zhangrui0214@cdu.edu.cn, 315024451@qq.com and 387680271@qq.com

Keywords: MXenes, MAX phase, tribology, 2D materials, Ti$_3$C$_2$

Abstract

Ti$_3$C$_2$ layers with a layered two-dimensional structure are synthesized by immersing a precursor Ti$_3$AlC$_2$ with hydrofluoric acid solution. The microstructure of Ti$_3$C$_2$ layers is analyzed by SEM, XRD, Raman and AFM. Additionally, the tribological behavior of Ti$_3$C$_2$ layers is investigated at various loads and sliding speeds by sliding against Si$_3$N$_4$ balls on a UMT-2 tribometer. In comparison, the tribological behavior of Ti$_3$AlC$_2$ at various loads is tested under identical condition. The results indicate that the Ti$_3$C$_2$ layers have been successfully prepared and their thickness mainly distributes in the range of 2.3–3.1 nm. Moreover, the Ti$_3$C$_2$ layers exhibit better tribological behavior than its precursor - Ti$_3$AlC$_2$ in dry sliding. It is expected that the Ti$_3$C$_2$ layers will be applied as a solid lubricant additive for other materials.

1. Introduction

MAX phases combine the advantages of both metals and non-metals. They have a big family with about 150 members [1]. As one member of this huge family, Ti$_3$AlC$_2$ inherits the layered hexagonal with P6$_3$/mmc symmetry, where the Ti layers are nearly closed packed, and the C atoms fill the octahedral sites. The Ti$_3$C$_2$ layers are, in turn, interleaved with layers of Al atoms [2]. When the Al layers are selectively etched away without disrupting the Ti-C bonds, then Ti$_3$C$_2$ layers with a two-dimensional (2D) character will be obtained. They were first reported in 2011 by M. Naguib et al [3]. Just like other nanosheets, the Ti$_3$C$_2$ layers have rich surface chemistries and high electronic conductivities and exhibit prominent performance in catalysis chemistry [4, 5] and energy storage systems [6–9]. Peng et al [10] have studied the unique lead adsorption behavior of 2D Ti$_3$C$_2$ layers. Additionally, they have the potential to be applied in biomedical [11, 12] and sensing [13, 14]. In the field of friction, the Ti$_3$C$_2$ layers have been used as additives in base oil and a possible mechanism has been put forward [15]. However, researches on the dry friction of the Ti$_3$C$_2$ layers are still blank.

To shed light on future material application, Ti$_3$C$_2$ layers on Ti$_3$AlC$_2$ were fabricated and characterized. Additionally, the tribological behavior of the Ti$_3$C$_2$ layers sliding against Si$_3$N$_4$ balls in air was investigated using a ball-on-disk tribometer at room temperature.

2. Material and methods

2.1. Preparation of Ti$_3$C$_2$

Polycrystalline Ti$_3$AlC$_2$ bulk (Φ 24 mm × 7.9 mm) was in situ synthesized by a solid-liquid phase reaction using hot press sintering stove in vacuum. A powder mixture of TiC, Ti and Al with a mole ratio of 1.8:1:1.1 were hot
pressed at 1400 °C and 25 MPa for 30 minutes in a graphite die. The purity and density of the as-prepared Ti₃AlC₂ was 98.9 vol.% and 97.4%, respectively. Its average grain size and micro-hardness was 13 μm and 4.66 GPa, respectively. After polishing treatment, the surface roughness (Ra) of the Ti₃AlC₂ bulk was approximately 0.26 μm.

The Ti₃AlC₂ bulk was immersed in a 40% concentrated HF solution at room temperature for 10 h. The product was then washed with ethanol several times, dried in vacuum at 70 °C for 12 h and the 2D Ti₃C₂ layer saturated by suitable ligands (such as F or –OH) covering on Ti₃AlC₂ was obtained.

In order to facilitate the examination of the microstructure of the Ti₃C₂ layers, some particles were mechanically obtained from the Ti₃C₂ layers covering on Ti₃AlC₂. They were subsequently washed by using ethanol for several times and dried in vacuum at 70 °C for 12 h.

2.2. Friction and wear test
The tribological tests were conducted on a reciprocating ball-on-disc UMT-2 tribometer (CETR, USA). The stroke was 5 mm in length. The test was carried out at room temperature with the Ti₃C₂ layers sliding against Si₃N₄ balls (Φ 3 mm) with a surface roughness of 0.05 μm. The sliding speeds were 0.02 and 0.1 m s⁻¹, respectively. The loads were 0.1, 0.5 and 1 N, respectively. In comparison, the precursor Ti₃AlC₂ was tested sliding against Si₃N₄ balls under identical conditions. Before each test, all discs and balls were ultrasonically cleaned in acetone. Each test was repeated at least 3 times. The friction coefficients were recorded automatically and then processed by Origin software.

2.3. Characterization
The phase composition of the Ti₃C₂ layers and original Ti₃AlC₂ was examined by x-ray diffractometer (XRD, D/Max-2400, Rigaku) using Cu Ka (λ = 0.15418 nm). XRD patterns were recorded in the 2θ range of 5–65° with a step size of 0.02° and a scan speed of 1° min⁻¹. Raman spectra of the Ti₃C₂ layers was carried out on Raman spectrometer (Renishaw, inVia) with an Ar laser (514.5 nm) as excitation source in the wavelength range of 100–1000 cm⁻¹. Surface morphology and its worn surface of the Ti₃C₂ layers was analyzed by using Scanning electron microscopy (SEM, JEOL JSM-5600LV), equipped with energy dispersive x-ray spectroscopy (EDS). The thickness of the 2D Ti₃C₂ nanocrystal, which was scattered on the surface of silicon wafer (10 × 10 mm²) cleaned by nitro hydrochloric acid, was measured by atomic force microscopy (AFM, Multimode 8, Bruker).

3. Results and discussion
3.1. Microstructure
XRD patterns of Ti₃AlC₂ and the Ti₃C₂ layers are shown in figure 1(a). Compared with Ti₃AlC₂, the diffraction peaks of the Ti₃C₂ layers are obviously broadened and weak. Raman spectra of Ti₃AlC₂ and the Ti₃C₂ layers are seen in figure 1(b). Compared with Ti₃AlC₂, peaks I, II and III of the Ti₃C₂ layers vanished, while peaks IV, V and VI merged, broadened, and downshifted. Such downshifting phenomena has been observed in Raman spectra of very thin layers of inorganic layered compounds [16]. The line broadening and the spectral shifts in the Raman spectra are in agreement with the broadened XRD profiles. Similar to Ti₃SiC₂ [17], peaks I to III in figure 1(b) can be assigned to Al-Ti vibrations, while peaks V and VI involve only Ti-C vibrations. The fact that the latter two peaks merge and exist after etching confirms both the mode assignments and, more importantly, the loss of Al from the structure. The above results are in agreement with [3]. SEM graph of the Ti₃C₂ layers is shown in figure 1(c). It can be seen from figure 1(c) that the obtained Ti₃C₂ layers showed an obvious 2D layered structure. The corresponding EDS (see figure 1(d) and table 1) data demonstrates that the Ti₃C₂ layers are composed of Ti, C, O and F with negligible Al. This finding is in accordance with [3].

Surface image and thickness measurement of Ti₃C₂ nanolayers analyzed by AFM are shown in figure 2. It can be seen from figure 2(a) that some defects (holes) are formed on Ti₃C₂, which may result from the prolonged HF treatment [18]. The thickness of Ti₃C₂ was manually measured by counting at least 500 steps of the cross-sectional profile of the Ti₃C₂ layers (see figure 2(b)). It was proved that the thickness of the Ti₃C₂ layers mainly distributed in the range of 2.3–3.1 nm, accounting for 85% (see figure 2(c)).

3.2. Tribological properties
Tribological behaviors of Ti₃AlC₂ and the Ti₃C₂ layers at various loads sliding against Si₃N₄ balls with a reciprocating motion are shown in figure 3. When the load is 0.1 N, the friction coefficient of Ti₃AlC₂ has a large fluctuation with a running-in period of about 60 s. When the load is larger than 0.1 N, the fluctuation of the friction coefficient of Ti₃AlC₂ are obviously reduced. Moreover, with the increase of load, the average friction coefficient of Ti₃AlC₂ is slightly reduced. In comparison, the tribological behavior of the Ti₃C₂ layers is different from that of Ti₃AlC₂. When the load is 0.1 N, the friction coefficient of the Ti₃C₂ layers fluctuates to a certain
extent. When the loads are 0.5 and 1 N, the friction coefficient of the Ti₃C₂ layers are quite stable throughout the sliding. Additionally, the average friction coefficient of the Ti₃C₂ layers increases with the increase of load. At lower loads, the friction coefficient of the Ti₃C₂ layers is lower than that of Ti₃AlC₂. It is speculated that larger load makes direct contact of Ti₃AlC₂ with Si₃N₄ in the end of the sliding, which is demonstrated by the scratch on the wear track of the Ti₃C₂ layers (see figure 5(a)). Such phenomena may be resulted from the wear out of the Ti₃C₂ layers on Ti₃AlC₂. Therefore, similar friction coefficients in the latter part of the friction curves are observed for Ti₃AlC₂ and the Ti₃C₂ layers under the load of 1 N. It is deduced that Ti₃C₂ is a potential solid-lubricating material.

The tribological behavior of the Ti₃C₂ layers at different sliding speeds is studied, which is shown in figure 4. As shown in figure 4, the friction coefficient of Ti₃C₂ is only slightly sensitive to the sliding speeds. Compared with the curve (black line) at a sliding speed of 0.02 m s⁻¹, the curve (red line) at a sliding speed of 0.1 m s⁻¹ has a shorter running-in period and lower steady friction coefficient with a similar trend. It is speculated that higher sliding speed promotes Ti₃C₂ to behave lower friction to a certain extent.

The wear morphology of Ti₃C₂ layers is shown in figure 5. As seen in figure 5(a), the wear of the Ti₃C₂ layers during sliding is obvious with a distinct wear track. From the local magnification of the wear track (see

Table 1. Analysis of element type and content of Ti₃C₂ corresponding to figure 1(d).

| Elements | Apparent concentration | wt% | Atomic percentage |
|----------|------------------------|-----|-------------------|
| C        | 9.54                   | 15.92 | 29.77 |
| O        | 7.62                   | 13.82 | 19.40 |
| F        | 26.75                  | 24.50 | 28.96 |
| Al       | 1.46                   | 1.15 | 0.96 |
| Ti       | 73.38                  | 44.61 | 20.91 |
| Total    | 100.00                 | 100.00 | 100.00 |

Figure 1. Composition and structure of Ti₃AlC₂ and Ti₃C₂. (a) XRD patterns, (b) Raman spectra, (c) SEM graph of Ti₃C₂, and (d) its corresponding EDS data.
figure 5(b), some fine debris are found. It is not deniable that the as-synthesized Ti₃C₂ layers are easy to wear. The unsatisfactory wear resistance of Ti₃C₂ is perhaps owing to the big volume shrinkage of Ti₃C₂ (approximately 19%) [3] and the weak interaction between Ti₃C₂ and its precursor. To sum up, the Ti₃C₂ layers behave lower friction coefficients than Ti₃AlC₂, whereas its wear resistance is unsatisified. It is more applicable for lubricating additives or bulk materials.

4. Conclusions

Microstructure and tribological property of the Ti₃C₂ layers have been investigated in this paper. Its microstructure is examined by SEM, XRD, Raman and AFM. The results show that the Ti₃C₂ layers have a layered two-dimensional structure with the thickness mainly in the range of 2.3–3.1 nm. The layered structure of

![Figure 2](image)

**Figure 2.** Ti₃C₂ scattered on Si wafer. (a) AFM, (b) Cross-sectional profile corresponding to (a) and (c) Thickness distribution.

![Figure 3](image)

**Figure 3.** Frictional behaviors of Ti₃AlC₂ and Ti₃C₂ at various loads (0.1, 0.5 and 1 N, respectively) with a sliding speed of 0.02 m s⁻¹.
Ti$_3$C$_2$ makes it exhibit lower friction under various loads and sliding speeds. It is predicted that the Ti$_3$C$_2$ layers can be applied as a solid lubricant additive of other materials, which needs further exploration.

**Acknowledgments**

The author acknowledges the financial support from the Youth Foundation of Changzhou Institute of Technology (YN1711).

**Data availability statement**

All data that support the findings of this study are included within the article (and any supplementary files).

**ORCID iDs**

Fuyan Liu [https://orcid.org/0000-0002-1667-5139](https://orcid.org/0000-0002-1667-5139)
References

[1] Sokol M, Natu V, Kota S and Barsoum M W 2019 On the chemical diversity of the MAX phases Trends in Chemistry 1 210–23
[2] Barsoum M W 2000 The M_{1+x}AX_{1-x} phases: a new class of solids; thermodynamically stable nanolaminates Prog. Solid State Chem. 28 201–8
[3] Naguib M, Kurtoglu M, Presser V, Lu J, Niu J J, Heom M, Hultman L, Gogotsi Y and Barsoum M W 2011 Two-dimensional nanocrystals produced by exfoliation of Ti_{3}AlC_{2} Adv. Mater. 23 4246–53
[4] Xie X H, Chen S G, Ding W, Nie Y and Wei Z D 2013 An extraordinarily stable catalyst: Pt NPs supported on two-dimensional Ti_{3}C_{2}X_{2} (X = OH, F) nanosheets for oxygen reduction reaction Chemical Communication 49 10112–4
[5] Morales-Garcia A, Calle-Vallejo F and Illas F 2020 MXenes: new horizons in catalysis ACS Catal. 10 13487–503
[6] Naguib M, Halim V N, Lu J, Cook K M, Hultman L, Gogotsi Y and Barsoum M W 2013 New two-dimensional niobium and vanadium carbides as promising materials for Li−ion batteries Journal of the American Chemical Society 135 15966–9
[7] Lukatskaya M R et al 2013 Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide Science 341 1502–5
[8] Ming F W, Liang H F, Huang G, Bayhan Z and Alshareef H N 2021 MXenes for rechargeable batteries beyond the lithium-ion Adv. Mater. 33 e2004039
[9] Hu M, Zhang H, Hu T, Fan B, Wang X and Li Z 2020 Emerging 2D MXenes for supercapacitors: status, challenges and prospects Chem. Soc. Rev. 49 6666–93
[10] Peng Q M, Guo J X, Zhang Q R, Xiang J Y, Liu B Z, Zhou A G, Liu R P and Tian Y J 2014 Unique lead adsorption behavior of activated hydroxyl group in two-dimensional titanium carbide J. Am. Chem. Soc. 136 4113–6
[11] Chen K. et al 2018 Strong and biocompatible poly (lactic acid) membrane enhanced by Ti_{3}C_{2}Tz (MXene) nanosheets for guided bone regeneration Mater. Lett. 229 114–7
[12] Huang K, Li Z, Lin J, Han G and Huang P 2018 Two-dimensional transition metal carbides and nitrides (MXenes) for biomedical applications Chem. Soc. Rev. 47 5109–24
[13] Adepu V, Kamath K, Mattela V and Sahatiya P 2021 Laser-assisted gaussian microstructure patterned PDMS encapsulated Ti_{3}C_{2}T_{x} (MXene) based pressure sensor for object and touch detection IEEE Sens. J. 21 16547–53
[14] Lee S H, Eom W, Shin H, Ambade R B, Bang J H, Kim H W and Han T H 2020 Room-temperature, highly durable Ti_{3}C_{2}T_{x} MXene/graphene hybrid fibers for NH3 gas sensing ACS Appl. Mater. Interfaces 12 10434–42
[15] Zhang X H, Xue M Q, Yang X H, Wang Z P, Luo G S, Huang Z D, Sui X L and Li C S 2015 Preparation and tribological properties of Ti_{3}C_{2}(OH)_{2} nanosheets as additives in base oil RSC Adv. 5 27627–33
[16] Rao C N R, Subrahmanyan K S, Ramakrishna Matte H S S, Abdulhakeem B, Govindaraj A, Das B, Kumar P, Ghosh A and Late D J 2010 A study of the synthetic methods and properties of graphenes Sci. Technol. Adv. Mater. 11 054502
[17] Spanier J E, Gupta S, Amer M and Barsoum M W 2005 Vibrational behavior of the M_{1+x}AX_{1-x} phases from first-order Raman scattering (M = Ti, V, Cr, A = Si, X = C, N) Physical Review B 71 012103
[18] Naguib M, Mashitlar O, Carle J, Presser V, Lu J, Hultman L, Gogotsi Y and Barsoum M W 2012 Two-dimensional transition metal carbides ACS Nano 6 1322–31