Tribological Properties of Ti_3SiC_2

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The present contribution reports the unlubricated friction and wear properties of Ti_3SiC_2 against steel. The fretting experiments were performed under varying load (1–10 N) and the detailed wear mechanism is studied using SEM-EDS, Raman spectroscopy, and atomic force microscopy. Under the selected fretting conditions, Ti_3SiC_2/steel tribocouple exhibits a transition in friction as well as wear behavior with coefficient of friction varying between 0.5 and 0.6 and wear rate in the order of 10^{-5} $mm^3 \cdot (N \cdot m)^{-1}$. Raman analysis reveals that the fretting wear is accompanied by the triboxidation with the formation of TiO_2, SiO_2, and Fe_2O_3. A plausible explanation for the transition in friction and wear with load is proposed.

I. Introduction

In recent times, ternary carbides[1] and silicides[2] have received wider attention in the materials community. The research on ternary carbides, in particular Ti_3SiC_2, was triggered since the seminal work carried out by Barsoum and El-Raghy.[3] Monolithic ternary silicon carbide has potential structural applications, because of its low density (4.53 g/cc), high fracture toughness (7–9 $MPa \cdot m^{1/2}$), and high Young's modulus (325 GPa).[4] Barsoum[5] identified that this ternary carbide represents a new class of solids and it can be described as thermodynamically stable nanolaminates, which exhibit both metallic and ceramic features. Ti_3SiC_2 has low hardness ($\sim$5 GPa), even lower than fully hardened steel ($\sim$7 GPa). Although different processing routes to obtain dense Ti_3SiC_2 have been reported and the mechanical properties have been measured,[6,7] limited work has been carried out to evaluate their potential in tribological applications.

Myhra *et al.*[8] measured a low kinetic friction coefficient (μ) of 0.002 at 25 nN lateral force for the basal planes of Ti_3SiC_2, using the lateral force microscopy (LFM) method. They also reported a steady-state coefficient of friction (COF) of $\sim$0.12 for a polycrystalline Ti_3SiC_2 rubbed against a lightly peened stainless-steel sheet at 0.15–0.9 N load. Barsoum measured[9] a steady-state COF of around 0.8 in case of Ti_3SiC_2/steel tribocouple under 5 N load and observed that the frictional response is independent of grain size (5–100 μm). Zhang *et al.*[10] reported that the friction of self-mated Ti_3SiC_2 tribocouple is $\sim$1.16–1.43 and that of Ti_3SiC_2/diamond is around 0.1 under varying loads of 0.98–9.8 N. In their research, Ti_3SiC_2 ceramic exhibited a rather low friction coefficient during dry sliding against diamond, because of the formation of a self-lubricating film. All the literature results are mainly based on the pin-on-disk measurements of the tribological behavior of Ti_3SiC_2, but no work has been carried out to understand the wear mechanism of Ti_3SiC_2 under fretting mode (I) contact.

To this end, the aim of this work is to investigate the fretting damage processes of Ti_3SiC_2 in contact with steel, under varying load. The details of the wear mechanism have been studied using scanning electron microscopy (SEM), atomic force microscopy (AFM), and Raman spectroscopy.

II. Experimental Procedure

In the present study, Ti_3SiC_2 was used as the flat material (moving) and commercial bearing steel balls of 8.02 mm (0.32 in) in diameter were used as the counterbody (stationary). The Ti_3SiC_2 specimens were prepared from the powder mixtures containing appropriate stoichiometric amounts of $TiC_{0.67}$ and Si (325 mesh, 99.99%) powder. The densification was carried out by hot pressing at 1420°C for 90 min under Ar atmosphere at 25 MPa pressure to obtain a density of 4.5 g/cc ($\sim$98% ρ_{th}). Following this, the larger disk specimens were machined to disks of 12 mm in diameter and 2 mm in thickness. The test surface of the disks was smoothly polished down to an $\sim$0.15 μm surface finish. Figure 1 represents a typical SEM micrograph of Ti_3SiC_2, etched in 1:1:1 by volume $HF:HNO_3:H_2O$ solution. The presence of large elongated Ti_3SiC_2 grains and the small amount of TiC (bright contrast) can be clearly observed. The volume fraction of TiC in the investigated Ti_3SCi_2 is found to be 13.7.

A ball-on-disk-type fretting tribometer has recently been fabricated and used in the present study. The use of this equipment has also been reported in some of our recent research.[11,12] Fretting is defined as a linear relative tangential displacement sliding at a constant normal load.[13] The computerized fretting tester has two transducers: an inductive displacement transducer sensing the movement of the flat sample (moving) and a piezoelectric transducer attached to the loading arm, which monitors friction force. The COF is obtained from the on-line measured tangential force. Before each test, the specimens and ball were ultrasonically cleaned with acetone. The fretting wear experiments were carried out with varying loads (1–10 N) at a constant testing duration (100 000 cycles), at

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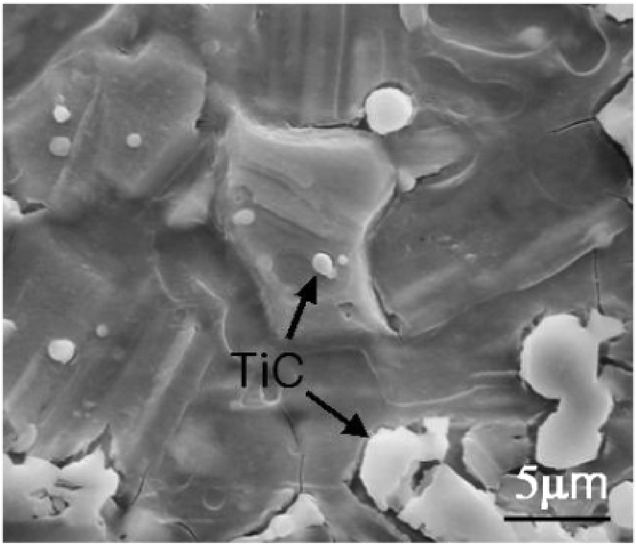


Fig. 1. Scanning electron microscopy image revealing the hot-pressed microstructure of Ti_3SiC_2, polished and etched. Note the presence of large elongated Ti_3SiC_2 grains and the small amount of TiC (bright contrast).

constant frequency (8 Hz) and constant displacement stroke (100 µm). Furthermore, detailed morphological investigation and wear mechanism were studied by SEM, AFM (AFM, Molecular Imaging, Pico-SPM I), and Raman Spectroscopy (Spectra Physics, 1877E Triplemate). The wear volume of the cleaned worn surface is calculated using a laser surface profilometer (Perthometer PGK-120, Mahr GmbH, Germany). The wear volume, measured using a laser surface profilometer, is normalized with respect to normal load and total sliding distance (number of cycles $\times$ displacement stroke $\times$ 2). To obtain the topography and roughness parameters, the worn surfaces were scanned after testing at 6 and 8 N. After performing the worn surface analysis, the fretted zone was cut by diamond cutter along the centerline and the cross-section was polished down to $\sim$0.1 µm. The transverse cross-sections were polished and Vickers hardness (load 0.98 N) was measured in the subsurface region after testing at selected fretting conditions.

III. Results and Discussion

In order to evaluate the friction and wear properties of Ti_3SiC_2, the fretting experiments are conducted with varying load while maintaining other parameters (sliding distance, frequency) constant. The obtained steady-state COF and wear rate are compared with the literature data, as recorded with Ti_3SiC_2 in Table I. The COF and wear rate data of present investigation are shown in Fig. 2. From the present experimental results, it is clear that the friction behavior is strongly dependent on normal load. The experimental data reveal that the steady-state COF of Ti_3SiC_2/steel couple increases from 0.55 to 0.62, as load is increased from 1 to 6 N under the selected testing parameters. However, a decrease in COF from 0.62 to 0.5 is noted as load is further increased to 8 N or more. A slightly different trend can be observed while analyzing the wear rate data. At the lowest load regime (1 N), the specific wear rate is low and around 11×10^{-5} $mm^3 \cdot (N \cdot m)^{-1}$. The wear rate increases with load from 1 to 2 N, but does not vary much (22–23 $\times 10^{-5}$ $mm^3/N.m$) for a fretting load of 2–6 N. A clear increase in the wear rate is recorded for an increase in load to 8–10 N.

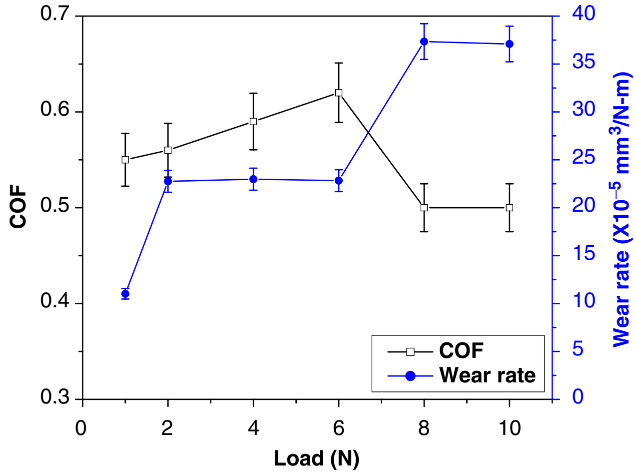


Fig. 2. The coefficient of friction and wear rate for Ti_3SiC_2 against steel at different loads. Fretting conditions: 100 000 cycles, 8 Hz frequency, and 100 µm stroke length.

To this end, it can be noted that the COF of Ti_3SiC_2/steel, as measured by a pin-on-disk tribometer, is around 0.83 at 5 N load irrespective of grain size.[9] The average sliding wear rates were reported to be around 425×10^{-5} and 134×10^{-5} $mm^3 \cdot (N \cdot m)^{-1}$ for the fine- and the coarse-grain microstructure, respectively. However, under ambient and vacuum conditions, the LFM study along the basal plane of Ti_3SiC_2 indicates an ultra-low coefficient of friction 0.002 at a load of 25 nN.[10] In

Table I. Summary of the Friction and Wear Data Obtained with Ti_3SiC_2 Under Varying Test Conditions

Specimen	Counterbody	Contact	Load	COF	Wear rate (10^{-5} $mm^3 \cdot (N \cdot m)^{-1}$)	Reference
Ti_3SiC_2	Steel	Ball-on-disk	1 N	0.55±0.05	11±1	Present work
			2 N	0.56±0.05	23±2	
			4 N	0.59±0.05	23±4	
			6 N	0.62±0.05	23±6	
			8 N	0.50±0.05	37±4	
			10 N	0.50±0.05	37±5	
Ti_3SiC_2	—	LFM	25 nN	0.002†	—	Myhra *et al.*[8]
Ti_3SiC_2	Steel	Pin-on-disk	5 N	0.83	134–425	El-Raghy *et al.*[9]
Ti_3SiC_2	Ti_3SiC_2	Pin-on-flat	0.98 N	1.43	—	
			1.96 N	1.29		
			2.94 N	1.34		
			4.9 N	1.23		
			9.8 N	1.16		
	Diamond	Pin-on-flat	0.98 N	0.09		Zhang *et al.*[10]
			1.96 N	0.08		
			2.94 N	0.08		
			4.9 N	0.07		
			9.8 N	0.06		

LFM, lateral force microscopy; COF, coefficient of friction. †Along the basal plane of Ti_3SiC_2

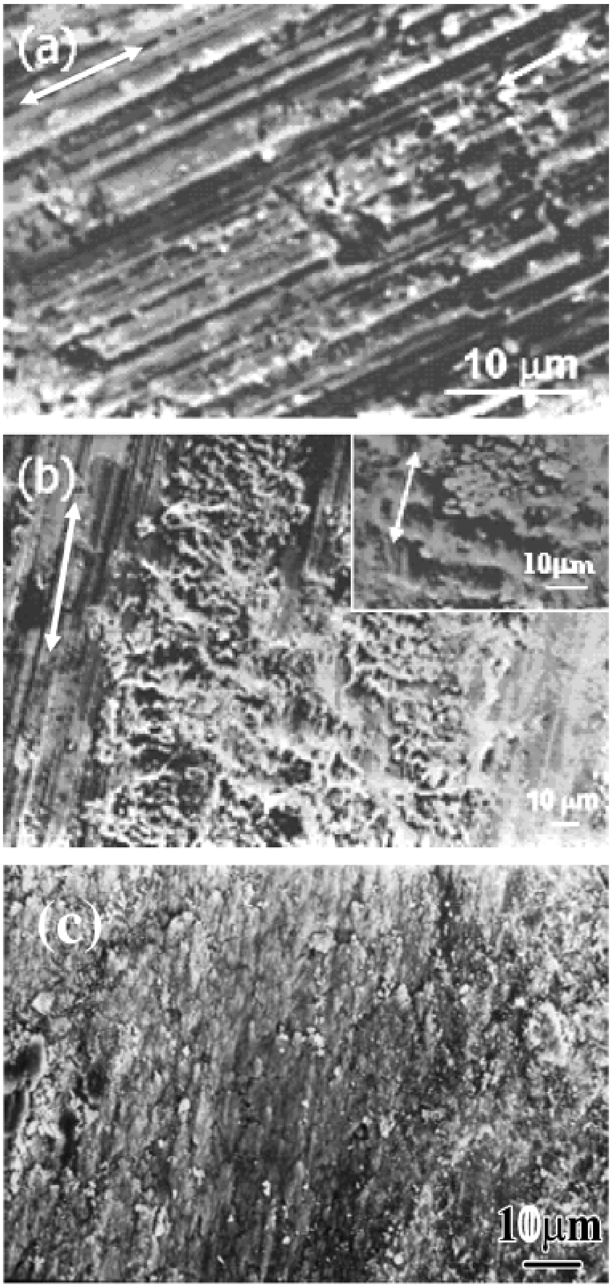


Fig. 3. Scanning electron microscopy images revealing the presence of deeper abrasive scratches of groove width around 2–3 μm at 1 N load (a) and extensive plastic deformation at 8 and 10 N load (b, c) on a Ti_3SiC_2 worn surface after fretting against bearing steel for 100 000 cycles. The details of the deformed tribolayer and debris particle are also shown in the inset of (b). The pointed arrow indicates the sliding direction.

this case, AFM results did not reveal enough evidence of wear rate and mechanism. In another study, Zhang *et al.*[8] measured a higher COF, varying between 1.16 and 1.43. However, a lower COF of <0.1 is recorded under a similar sliding condition for a Ti_3SiC_2/diamond tribocouple. The superior frictional behavior was explained in terms of lubricating efficiency of the diamond tribofilm. The lower COF, as measured in the present case, is because of the difference in contact configuration (pin-on-disk versus fretting) and operating parameters (sliding velocity).

SEM images (Fig. 3) of the worn surface topography are critically analyzed to understand the wear mechanisms. At a lower load (<6 N), the fretted surface is typically characterized by deeper abrasive grooves (Fig. 3(a)), which can be explained from the difference in hardness of Ti_3SiC_2 (~ 5 GPa) and steel (~ 7 GPa). The observed increase in COF at load <6 N is because of more severe abrasive action with normal load. At a higher load (>6 N), a distinct change in the morphology of the worn surface is recorded. Extensive plastic deformation, along with abrasive scratches, is commonly observed on the worn surfaces (Figs. 3 (b) and (c)). Also, the tribochemical layer is found to be fractured and non-protective. The wear debris (size <10 μm) particles are scattered at the different areas of the worn surface. The decrease in COF at a higher load can be explained by the transition from two- to three-body abrasion, caused by the wear debris formation. However, the increase in wear rate with an increase in load (see Table I) can be attributed to the additional contribution from tribochemical wear- and deformation-induced damage. Preliminary investigation to understand the subsurface damage is also carried out. After performing the fretting test at 8 N load, the fretted zone was cut in the transverse direction by a diamond cutter and the cross-section was polished down to ~ 0.1 μm. The transverse cross-sections were polished and Vickers microhardness (at 0.98 N load) was measured at the sub-surface region. Careful investigation of microhardness measurements nearer to the surface was carried out using a Leitz Wetzlar-8483 (Germany) microhardness tester at 0.98 N load applied for 10 s. The average of at least five microhardness tests measured at 20 μm from top surface is 612 ± 25 VHN. The hardness is observed to decrease to 440 ± 35 VHN just outside the fretted surface.

In order to obtain more information on the chemistry of the tribochemical layer, Raman spectroscopy analysis is carried out on Ti_3SiC_2 samples, fretted at 8 N (Fig. 4). Raman analysis shows evidence of the formation of Fe_2O_3, TiO_2, and SiO_2. On the basis of Raman results, it can be stated that tribo-oxidation of Ti_3SiC_2 at fretting contact occurs, leading to the formation of TiO_2 and SiO_2. Also, the steel ball severely oxidizes and the transfer of oxidized metallic debris takes place during fretting. The tribochemical oxidation during fretting can be described by the following reaction:

$$Ti_3SiC_2 + 6O_2 = 3TiO_2 + SiO_2 + 2CO_2 \tag{1}$$

The literature report confirms that the above reaction initiates at 900°C and the parabolic oxidation behavior in air between 900° and 1400°C leads to the formation of a distinct rutile and silica layer.[14] The activation energy of such a reaction is 370 ± 20 kJ/mol. However, under present fretting conditions of COF (~ 0.5), the activation energy (supplied by dissipation of frictional energy) will be high enough to activate the oxidation reaction at the frictional contacts even at a temperature lower than would occur under static condition, as reported elsewhere.[14]

The surface topographical analysis of the worn surfaces is also carried out by using AFM, and the roughness parameters are obtained. Figure 5(a) reveals that the worn surface is characterized by the severe abrasion, interestingly having grooves of different depths. Also, topographical features indicate that the

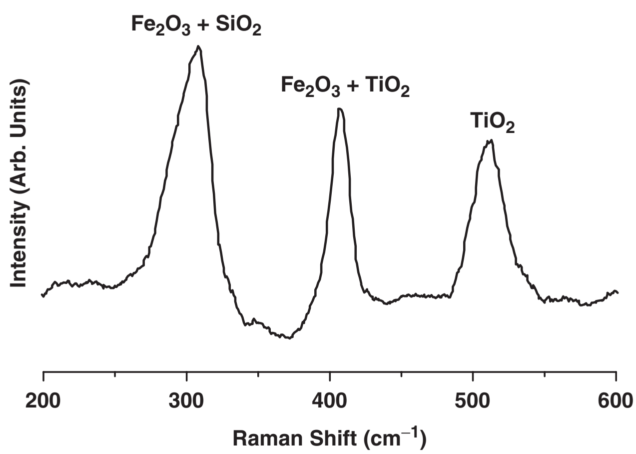
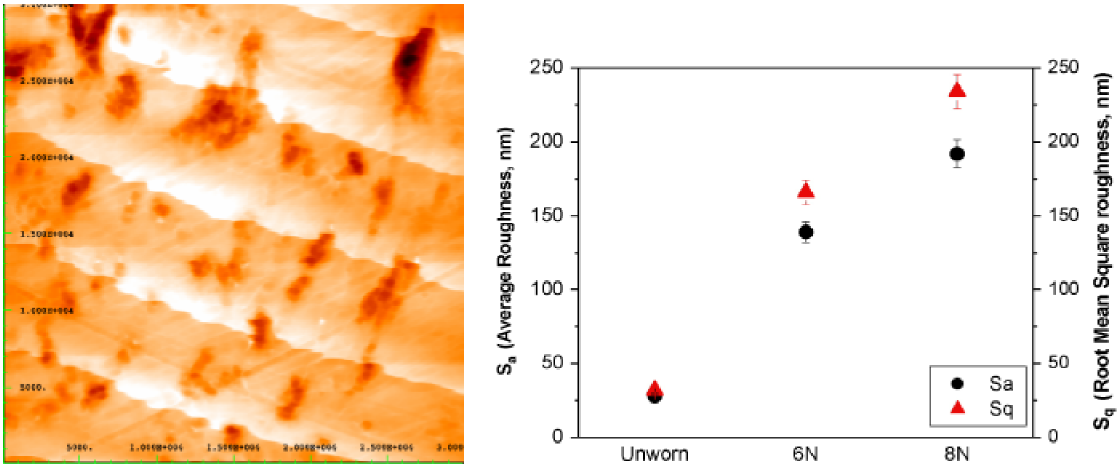


Fig. 4. Raman spectra obtained from the fretted surface on Ti_3SiC_2, worn against steel for 100 000 cycles at 8 N load.



(a) **(b)**

Fig. 5. Atomic force microscopy image of the worn surface topography of Ti_3SiC_2 after fretting against a steel ball at 8 N load (a). The roughness parameters obtained are plotted for unworn and worn surfaces, fretted at 6 and 8 N load (b).

deformation-induced damage is similar to that of wear of conventional metallic materials, dominated by plastic deformation. Therefore, it is to be understood that the combined effect of severe abrasion along with deformation-induced damage results in the removal of material occurring layer by layer. The obtained roughness parameters are plotted in Fig. 5(b). Observing Fig. 5(b), it is evident that S_a and S_q increase approximately five times after fretting at 6 N load and approximately eight times at 8 N load, when compared with unworn surface. This increase in roughness parameters indicates that the severity of wear also increases with load, leading to more rough surfaces.

IV. Conclusions

(a) The most important result is that a transition in COF and wear rate with load is measured. Under the investigated fretting conditions, the Ti_3SiC_2/steel tribocouple exhibits a high COF in the range of 0.5–0.6. At a higher load ($\geq$ 6 N), a decrease in COF is measured and this is believed to be because of the transition from two- to three-body abrasion.

(b) Ti_3SiC_2/steel exhibits a high fretting wear rate at a higher load ($>$6 N), which can be attributed to the tribochemical wear- and deformation-induced damage, occurring in addition to abrasion. Raman analysis indicates that the wear process is associated with the formation of TiO_2, SiO_2, and Fe_2O_3. AFM analysis reveals the increase in the surface roughness with an increase in load (6–8 N) applied during fretting, i.e. enhanced material damage at a higher load.

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