Oxidation layer in sliding friction surface of high-purity Ti_3SiC_2

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It has been shown in the last few years that the ternary carbide Ti_3SiC_2 has an excellent combination of properties in electric and thermal conductivity, refractoriness, oxidation resistance, damage tolerance, stress-strain characteristics and machinability [1–4]. Such unusual combination suggested it could be used as tribological materials. Myhra *et al*. [5] measured the kinetic friction coefficient of the basal planes of Ti_3SiC_2 to be as low as $2–5\times10^{-3}$. But they measured the friction coefficient of a polycrystalline Ti_3SiC_2 to be 0.12, when it is sliding against a lightly peened stainless steel sheet under a load of 0.15 to 0.9 N. El-Raghy *et al*. [6] investigated effects of grain size on the friction and wear for a high-purity Ti_3SiC_2 sample sliding against a 440C steel pin in pin-on-disk type tests, under 5 N normal load, 0.1 m/s sliding speed and 46.3 m sliding distance. The results showed that irrespective of the grain size, the steady friction coefficient is about 0.83, being almost 7 times the value measured by Myhra *et al*. [5]. Sun *et al*. [7] studied the friction and wear behavior of a Ti_3SiC_2-based material contained ~7 wt% TiC phase, using it as a disk sliding against a AISI 52100 steel pin in pin-on-disk tests, with the test parameters of 7 m/s sliding speed and four normal loads from 7.7 to 14.7 N. The results showed that the steady state friction coefficient increases from 0.4 to 0.5 with increase in the normal load applied. Such large difference in the measured friction coefficient is perhaps related with the friction surface status. In the previous works we found very limited literature on the friction and wear of Ti_3SiC_2, only Sun *et al*. [7] noted the presence of oxidation behavior. They observed that the worn surface of the Ti_3SiC_2-based disk was covered with very fine grains and partially compacted layers, which randomly distribute over the worn surface. They concluded that the debris made up of the Ti_3SiC_2 disk and steel pin materials was crushed into the fine grains, and sometimes compacted into layers on the Ti_3SiC_2 disk. However, whether the Ti_3SiC_2 material itself can be oxidized or not remains a question to date.

It has been observed [2, 8] that polycrystalline Ti_3SiC_2 is oxidizable in air, in the temperature range from 900 to 1400 °C. The scale that formed is dense, adhesive, and layered. The outer layer was pure TiO_2, and the inner layer consisted of a mixture of SiO_2 and TiO_2. This suggested that similar oxidation could also occur on the friction surface of a polycrystalline Ti_3SiC_2, because the real frictional temperature could be enough to induce the Ti_3SiC_2 oxidization when asperities of the Ti_3SiC_2 surface were severely impacted with that of the steel disk during sliding friction [9], though the apparent temperature of the entire Ti_3SiC_2 block may be lower. This idea was verified in the present study for the first time.

A high-purity polycrystalline Ti_3SiC_2 sample was prepared with the following processing. Commercial Ti (70 μm, >99.0% purity), Si (70 μm, >99.0% purity), C (graphite, 50 μm, >98.0% purity) and Al (70 μm, >99.5% purity) powders were mixed with a mole ratio of 3Ti:1Si:2C:0.2Al. The mixed powders were ball-milled for 8 hrs in ethanol solution by a rotary drum-type ball-miller. The ball-milled slurry was dried at 60 °C. The dried mixture was pulverized with a pestle, and screened through a 100-mesh sieve. The mixture powders were precompressed at 8 MPa in a graphite die, then hot-pressed in the self-same graphite die under 1450 °C and 25 MPa pressure for 2 hrs, with flowing argon gas. The heating rate was of 40 °C/min, and the cooling rate was of about 10 °C/min. The phase composition of the resultant products was analyzed by X-ray diffraction (XRD) with Cu K_α radiation, and the microstructure was observed by a scanning electron microscopy (SEM). The analyzed and observed results are shown in Fig. 1a and b, respectively. The content of Ti_3SiC_2 phase was estimated to be about 98 vol%, and the average grain size was estimated to be about 5 μm.

The frictional oxidation behavior of the Ti_3SiC_2 sample was examined using a block-on-disk type tester developed by Beijing Jiaotong University. The test principle is illustrated in Fig. 2. The Ti_3SiC_2 sample prepared was cut into several blocks with dimensions of 10 × 10 × 12 mm. A low carbon steel disk with dimensions of 300 mm in diameter and 10 mm in thickness was used as the counterpart sliding against the Ti_3SiC_2 block. Tests were conducted at room temperature within a relative humidity of 22–25%. The sliding speed was of 20 m/s, and the normal pressure was changed from 0.1 to 0.8 MPa. The friction surface was observed using the said scanning electron microscopy. The chemical status of the friction surface was analyzed using an energy dispersion spectroscopy (EDS) equipped in the scanning electron microscopy.

A general fact we found from the present tests is that all friction surfaces of the Ti_3SiC_2 blocks were covered by a layer consisting of the frictional products, and that the compactness and roughness of the layer depended on the normal pressure applied. Fig. 3a and b are typical SEM photographs exhibiting the friction surfaces of the Ti_3SiC_2 blocks, which underwent 24 000 m sliding distance under 0.2 and 0.8 MPa normal pressures, respectively. As could been seen, the layer formed under 0.2 MPa was partially compact, and its surface looked

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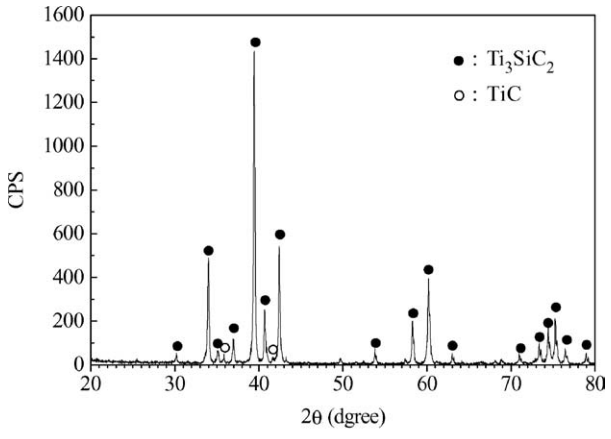
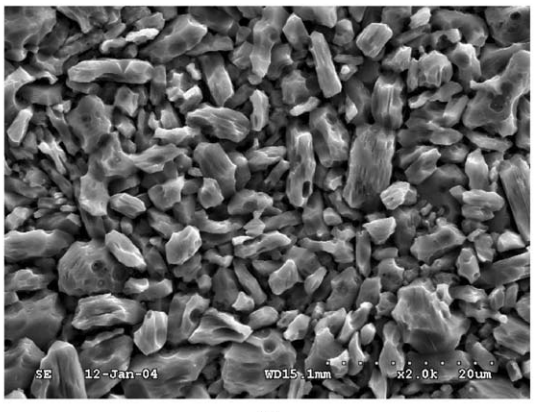


(a)



(b)

Figure 1 Essential attributes of the Ti_3SiC_2 sample prepared in the present study: (a) X-ray pattern and (b) SEM microphotograph.

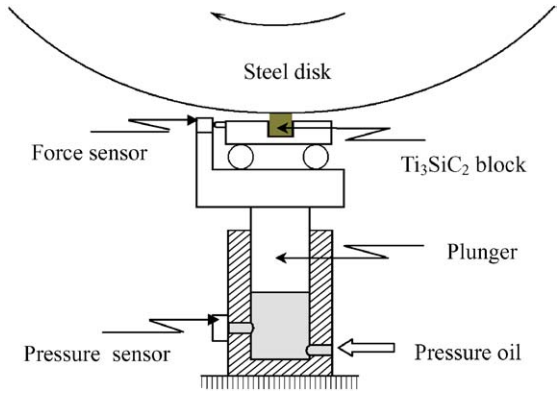
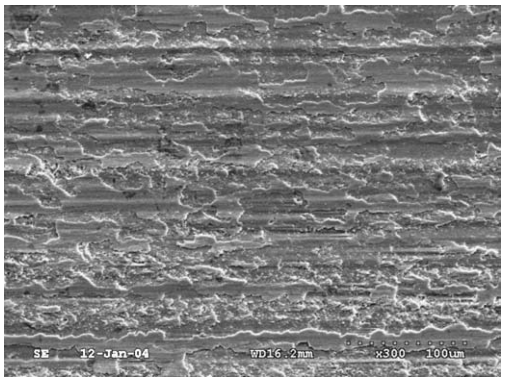
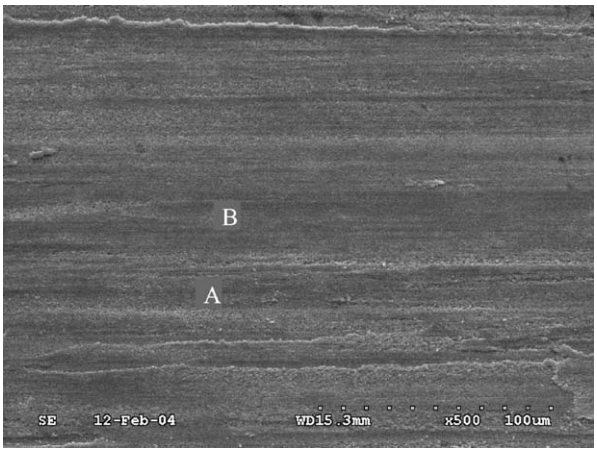


Figure 2 Diagram illustrating the block-on-disc type friction tester used in the present study.



(a)



(b)

Figure 3 SEM microphotographs of the friction surface of the Ti_3SiC_2 blocks, which underwent 24 000 m sliding distance under the normal pressures: (a) 0.2 MPa and (b) 0.8 MPa, respectively.

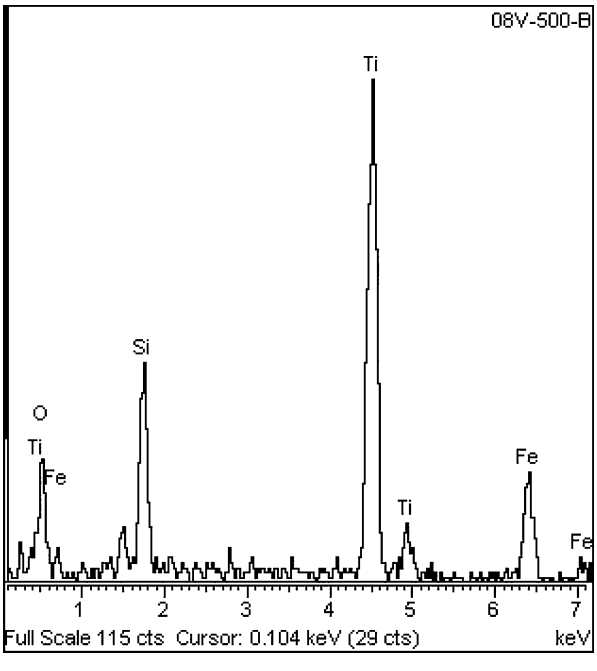


Figure 4 EDS pattern of the layer in the position marked by "B" in Fig. 3b.

quite rough. In contrast, the layer formed under 0.8 MPa was quite compact, and its surface was relatively smooth. Such frictional layer was first found in the friction surface of a high-purity Ti_3SiC_2 sample, and no similar status has been observed in the previous studies [5–7]. To understand the attributes of the layer, its chemical composition was analyzed by the EDS. It was found that the diffraction patterns obtained from different areas of the friction surface are almost identical, for instance, for the positions marked by A and B in Fig. 3b. The pattern shown in Fig. 4 is a representative result. There is no doubt that the layer contained some oxides, since there was high oxygen content. The presence of oxygen would be related to the oxidization of the iron transferred from the steel disk, as its lower oxidation resistance. However, the more important fact we noted is that the layer contained higher Ti and Si but no C, as shown in Fig. 4. This clearly indicates that the Ti_3SiC_2 has been decomposed and oxidized into titanum oxide

and silicon oxide on the friction surface. In terms of this analyzed result it can be concluded that the layer must be composed of the mixture of titanum oxide, silicon oxide and ferric oxide. For further clarity of the morphology of the layer, the XRD analysis was performed several times for the friction surface shown in Fig. 3b. However, no considerable diffraction peaks indicating the said oxides were found from the XRD patterns. This means that the layer would be composed of an amorphous mixture of the oxides. It is also worth noting that the layer seems to be quite soft in comparison with the counterface of the steel disk, since the rubbing tracks on the surface of the layer were so long as to cross the entire sliding surface, as shown in Fig. 3b.

In conclusion, the present work first demonstrated the presence of an oxide layer in the sliding friction surface of the high-purity Ti_3SiC_2 sample. The layer was identified to be composed of amorphous titanum oxide, silicon oxide and ferric oxide. The compactness and roughness of the layer changed with the normal pressure applied. More work is in progress to investigate the mechanism and influencing factors on the forming and damaging of the layer, and its effects on friction and wear behaviors.

Acknowledgments

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