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Oxide-based tribofilms and tribological behavior of self-mated Ti_3SiC_2 lubricated by PbO powders at high temperatures in nitrogen flow

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ABSTRACT

The friction and wear of self-mated Ti_3SiC_2 under unlubricated condition and lubrication of PbO powders from room temperature to 700 °C in a nitrogen flow are studied. The results show that compared to unlubricated condition, the friction coefficient of self-mated Ti_3SiC_2 under lubrication of PbO powders decreases from 0.9 to 0.3–0.5 and the wear rates for pin decreases from 10^{-2}–10^{-3} to 10^{-5}–10^{-7} mm^3/N m. The SEM and Raman results indicate the microstructure and chemical composition of tribofilm at high temperatures have a strong effect on the friction and wear of self-mated Ti_3SiC_2 under lubrication of PbO powders. The composition of tribofilm varies with tribochemical and thermal reactions happening between PbO and SiO_2/TiO_2 on the tribosurface. The composition of tribofilms are analyzed to be PbO at room temperature, PbO and Pb_3O_4 at 400 °C, and $PbTiO_3$ and $PbSiO_3$ at 700 °C. The $PbSiO_3$ is formed by tribochemical reaction while it cannot be formed under thermal condition.

1. Introduction

The Ti_3SiC_2 is a representative of MAX phases which are ternary carbides and nitrides with a layered hexagonal structure [1]. The Ti_3SiC_2 comprises characteristics of ceramic and metal, such as high mechanical properties, oxidation resistant at high temperature (over 1000 °C), anti-thermal shock and good machinability, etc. It is expected the Ti_3SiC_2 is able to be used to replace PS304 coating as a journal material for aerodynamic compliant foil bearings [2,3]. The first report on the properties of Ti_3SiC_2 suggested that it felt lubricious [4], which led Myhra et al. to study its tribological properties using a lateral force microscope [5]. They found the basal planes of Ti_3SiC_2 indeed had ultra-low coefficients of friction, μ ($2–5\times10^{-3}$); but the μ of non-basal planes was much higher (0.1). The tribological behaviors of coarse- and fine-grained polycrystalline Ti_3SiC_2 samples showed a high μ of 0.8 and the wear rates (WRs) of 10^{-3} mm^3/N m for both samples [6,7]. Tribological behavior was quite different when Ti_3SiC_2 was sliding against different materials. Zhang et al. [8] found that the μ of the self-mated Ti_3SiC_2 was higher than 1.0 because of adhesion and abrasion. But when against diamond the μ was lower than 0.1 due to a self-lubricating film formed on the surface of Ti_3SiC_2. Other investigations conducted at room temperature also found the layers of tribo-oxides on the surface of Ti_3SiC_2, which lead to lower friction and/or higher wear resistance [9–12]. Gupta et al. reported the tribological behavior of selected MAX phases including Ti_3SiC_2 against Ni-based superalloys at 550 °C [13,14]. The low WRs (10^{-6} mm^3/N m) and μ (0.4) were attributed to the tribo-oxidation products of Ni-alloy. Ren et al. studied the dry sliding behavior of Ti_3SiC_2 against Ni–Cr–Ti alloys from ambient up to 600 °C [15] and found that the oxide films of Ti on Ni–Cr–Ti alloy were effective in reducing friction and enhancing wear resistance. Ren et al. also investigated the tribological behavior of WC-based cermet/Ti_3SiC_2 tribo-pair at elevated temperatures [16] and found that the tribo-physical changes and tribo-chemical reactions including complex reaction and oxidations were induced by frictional heat combined with high environmental temperature. Gupta et al. classified the different tribofilms according to the source of tribo-reaction during sliding process between MAX phases and their tribo-pairs into four main categories [17]. To summarize, although the Ti_3SiC_2 has a layered structure, which is similar to that of graphite and MoS_2, it is not self-lubricious [17]. The tribological behavior of Ti_3SiC_2 depends largely on the oxidation of itself or the counter-face materials [7,9–12,17].

Hai has found that, below 500 °C, the friction coefficient and wear rates of self-mated Ti_3SiC_2 are as high as 0.9 and 10^{-3} mm^3/N m, respectively [18]. With the increasing of temperature, both

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friction and wear decrease. Above 700 °C, the friction coefficient and wear rates decrease to about 0.5 and 10^{-6} $mm^3/N\,m$, respectively. It can be seen that the tribological behavior of Ti_3SiC_2 needs to be improved at temperature below 500 °C.

The oxide powders, such as Fe_2O_3, SnO, CuO, Bi_2O_3, ZnO, PbO etc., have been widely used as solid lubricants [19–22]. An artificial supply of oxide particles accelerates the formation of a protective tribofilm thus reducing friction and wear [22]. The lubrication mechanism is due to the formation of a compacted oxides layer which behaves as a stress reducer [19]. In this paper, the friction and wear properties of the self-mated Ti_3SiC_2 lubricated by PbO powders from ambient temperature to 700 °C are studied. The interaction mechanism between the introduced oxides and tribo-surface of Ti_3SiC_2, which include tribo-chemical reactions and thermal reactions are studied. In order to avoid the interference from the tribo-pair, the self-mated contact condition is selected. Raman analysis of the composition of the tribofilm formed on the worn surfaces is used to interpret their influences on the tribological behavior of self-mated Ti_3SiC_2 lubricated by PbO powders at high temperatures. The basic results are expected to provide some references in the synthesis of self-lubricating Ti_3SiC_2-based composites.

2. Experimental

2.1. Material

The Ti_3SiC_2 samples are prepared using an in situ hot pressing/solid–liquid reaction process. The initial powders are Ti, Si, graphite and Al powders (3.1 mol%, as the sintering additive) [15]. Ti, Si, and graphite powders with stoichiometric quantities as well as Al powders are weighed and ball-milled, finally hot-pressed at 1450 °C under 25 MPa in a graphite die. The as-synthesized Ti_3SiC_2 samples contain less than 3 wt% TiC, which is determined by XRD (D/MAX-2400, Rigaku Corporation, Japan). The physical and mechanical properties are shown in Table 1. The commercial PbO powders (analytical pure) are used as the solid lubricant in the friction and wear test. The basic data of PbO are listed in Table 2. The purity of nitrogen gas is more than 99%.

2.2. Friction and wear test

The friction and wear tests are conducted on a high temperature unidirectional pin-on-disk tribometer (THT04015, CSEM Instrument Ltd., Switzerland). The pictures of tribo-meter and schematic diagram contact pattern are shown in Fig. 1. The hemispherically tipped Ti_3SiC_2 pin slides against a disk of the same material. The radius of the pin tip is 3 mm. The size of the disk is φ 25 mm × 8 mm. The surfaces of disks are polished to a 3 μm diamond finish and the pins are polished by silicon carbide and metallographic abrasive paper. Both pins and disks are cleaned ultrasonically in ethanol and dried prior to testing. The testing temperatures are room temperature, 200, 400, 600 and 700 °C. The sliding velocities are in the range of 0.01–1 m/s. The normal load are in the range of 1–10 N. The rotation radius and duration of the test are 6.00 mm and 30 min, respectively. All the tests are conducted in a nitrogen flow and each test is repeated three times.

Table 1
Physical and mechanical properties of Ti_3SiC_2 [18].

Properties	Density ($g\,cm^{-3}$)	Young's modulus (GPa)	Vicker's hardness (GPa)
Specification	4.388	331	6.3

Table 2
Basic data for PbO.

Lubricants	Crystal structure	Particle size	Melting point (K)	Mohs hardness
β-PbO	Orthorhombic system	–400 mesh	1159	2

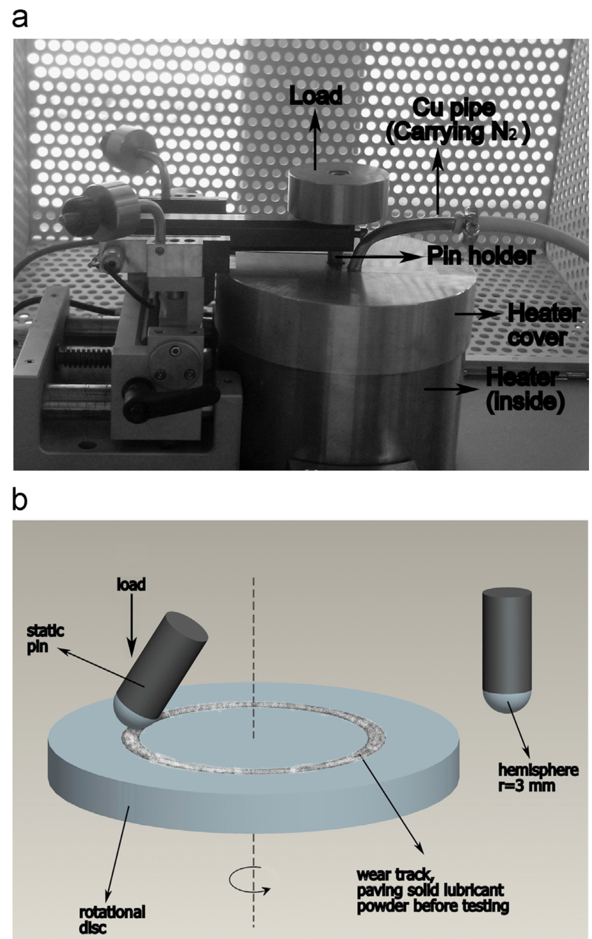

Fig. 1. Pictures of tribo-meter: (a) tribo-meter of high temperature and (b) schematic diagram contact pattern.

The nitrogen flow is used to protect the Ti_3SiC_2 surface from oxidization. As there are tribo-oxides of Ti_3SiC_2 on the interface in air [18], it is impossible to identify the lubrication effect of the introduced oxides. The inlet of the nitrogen flow is above the disk. The flux of nitrogen is 5 L/min during the draining air stage and 10 L/min during sliding. The ventilation mode is as follows. At room temperature, the nitrogen flow is ventilated for 10 min before the friction and wear test. After the test is finished, the nitrogen flow is stopped ventilating. At 100–300 °C, the nitrogen flow is started to ventilate for 10 min before the temperature reaches the set value. After the test is finished, the nitrogen flow is stopped ventilating. At 400–700 °C, the nitrogen flow is started to ventilate at 300 °C. After the test is finished, the nitrogen flow is stopped ventilating when the temperature decreases to 300 °C. The temperature of ventilating and stopping the nitrogen flow is chosen to be 300 °C, for above this temperature the thermal oxidation cannot be neglected [18].