COMPARISONS OF TRIBOLOGICAL PROPERTIES OF TI(C,N)/SIC IN WATER AND SEAWATER*

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Abstract

Ti(C,N)-based cermets offer good high temperature strength, perfect chemical stability, excellent wear resistance, and relativly better machinability. In the present work, the tribological behaviors of Ti(C,N)/SiC sliding pairs lubricated in water and seawater were evaluated using a ball-on-disk tribometer. The experimental results show that a relatively low friction coefficient (about 0.025) can be obtained when lubricated with artificial seawater at the sliding speed of 200 mm/s, while the date is about 0.2 in purified water. The wear surface profiles and the lubricants collected after running-in process for the high/low friction conditions were compared. In addition, the effect of salt molar concentration of the lubricant on the Ti(C,N)/SiC friction properties was investigated. It was found that the smooth and flat surface is the premise to gain the low friction. At the same time, the proper concentration of silica colloid, which is affected by the salt ions, is also an essential one. Moreover, the high sliding speed (200 mm/s) is beneficial to achieve low friction.

Keywords: Cermets; Friction; Boundary lubrication; Tribochemistry.

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* *Technical contribution to the 2nd International Brazilian Conference on Tribology – TriboBR 2014, November 3rd to 5th, 2014, Foz do Iguaçu, PR, Brazil.*

ISSN 2179-3956

1 INTRODUCTION

It is universally acknowledged that oil will occupy its absolute dominant position in lubrication area in the foreseeable future. By some estimates, world demand for lubricants will rise 2.6 percent annually to 41.7 million metric tons in 2015[1]. During the process of refining and expending such quantity of lubricants, many environmental issues must be considered, such as gas emissions and oil leaks. Exploring a kind of green lubricant is the common target of human beings. Water is a natural lubricant, which covers over 70 percent of the earth's surface and contains abundant resources. Adopting water as lubricant, we can achieve the true environmental sustainability, as well as in economic and social.

In the past decade, extensive interests have been given to the ceramic water lubrication since a very low friction coefficient (< 0.002) of self-mated Si_3N_4 was found in water lubrication[2]. After that, a large number of water lubrication studies had been performed on silicon based non-oxidation ceramics, such as Si3N4 and SiC[3-11]. The extremely low friction behavior of Si3N4 was confirmed by Xu et al. [3, 6] and Chen et al. [7, 12] in a series of studies and the low friction was only obtained at higher speeds and lower loads. Wong et al. [5] mapped out the effective range for water lubrication regions for four kinds of ceramics (SiC, Si3N4, Al2O3 and ZrO2) against themselves. The result showed that self-mated SiC had the largest effective region and is the best combination for water lubrication.

Although the self-mated Si3N4 and SiC in water have both shown the low friction coefficient, their industrial application has not been expanded to the expected level. Up to now, only SiC/SiC tribo-pair has successfully been used as water lubricated bearings or mechanical water seals[13]. It is often pointed out that the faults of ceramic material: low fracture toughness, low machining, high cost and so on.

Nowadays, cermets, especially Ti(C,N) have considerable interest because of their unique combination of properties such as high melting temperature, high hardness, wear resistance, relatively low coefficient of friction, high electrical and thermal conductivities[14-16]. At the same time, cermets are less expensive and their machinability has been somewhat improved compared with traditional ceramics.

Currently, Ti(C,N) cermets has attracted significant attention in the field of cutting tool materials, and thus, its tribological performance becomes one of the most important properties. Compared with ceramics, Ti(C,N) cermets exhibited excellent anti-wear property coupled with different counterparts[17], which resulted from the tribo-oxidative formation of so-called 'lubricious oxides'. Jeon et al.[18] studied the wear resistance of Ti(C,N) at high temperature of 873 K and it was found that the phase size and its distribution exerted a major impact on wear property. The influence of TiN content in Ti(C,N) cermets on tribological performance was studied by Cardinal et al.[15] and the cermets containing 10wt% of TiN presented the best friction coefficient and the lowest wear rate. During the dry sliding process, Córdoba et al. observed an increment in wear resistance when the hardness of the Ti(C,N) cermets increased[16]. The tribochemistry in dry sliding wear of TiCN-Ni-based cermets was studied by Kumar et al.[19] and the results revealed that the added secondary carbides influenced chemical interactions between different oxides and such interactions dominated the friction and wear behaviors.

In general, most of the previous studies on the tribological behavior of Ti(C,N) cermets were carried out at dry friction condition. Considering the excellent water lubrication properties of ceramics as mentioned above, what about the Ti(C,N) cermets? Can ultra-low friction coefficient also be obtained for cermets Ti(C,N) in

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water? Since the 70% of the earth's surface is covered by oceans, how about the friction properties of Ti(C,N) when operated in seawater? There is little knowledge about this. So in the work, compared with purified water lubrication, attention was paid on the tribological properties of Ti(C,N)-based cermets in seawater condition. And ceramic SiC was chosen as friction pair for its excellent water lubrication properties. Furthermore, the relation between friction properties and salt molar concentration of the lubricant was discussed also.

2 EXPERIMENTAL PROCEDURE

2.1 Specimen Preparation

The Ti(C,N) based cermets were fabricated by means of vacuum sintering. The composition and particle sizes of the raw materials were shown in table 1. The powders soaked in absolute ethanol were mixed by high energy ball milling for 24 h with the rotational speed of 250 rpm. The slurry mixture was dried and compacted in a steel die under uniaxial load of 270 MPa for 60 sec to give a circular disk of 32 mm in diameter. And then, the green body was sintered in vacuum at temperature up to 1400°C during 4.5 h.

Table 1. Composition and particle sizes of the raw materials of Ti(C,N) cermets

Powder	TiC		TiN		Ni	Mo	WC	Cr_3C_2	C
Particle size (μm)	2.5	20.0×10^{-3}	3.0	14.0×10^{-3}	1.7	3.2	4.5	3.4	5.5
Mass fraction (wt.%)	38.5	2.0	11.4	0.6	25.0	16.0	4.8	0.6	1.1

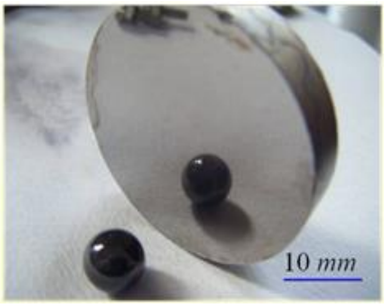

Fig.1 The image of SiC ball and Ti(C,N) disk

Figure 1 presents the tribo-pair image of Ti(C,N) disk and SiC ball. The final surface roughness Ra of Ti(C,N) disk is controlled at about 50 nm after grinding and polishing. The commercially available SiC ball, with a diameter of 8 mm, roughness Ra less than 14 nm is chosen as upper specimen (Shanghai Research Institute of Materials).

2.2 Friction Test

Friction tests were carried out using a ball-on-disk tester and Fig.2 shows the apparatus. The lower disk of Ti(C,N)-based cermets is fixed in a container, which is driven by a motor with an adjustable rotational speed. The stationary ball, held by an arm, pressed against the disk by the external dead weight. Lubricant is filled in the container, and the contact surface of the ball and disk is submerged in the liquid all through the test period. According to the strain of the arm caused by friction force, the coefficient of friction was continuously measured using an eddy current sensor and a personal computer controlled data acquisition system.

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Describe in detail the equipment and procedures used, which will allow the research to be reproduced by other researchers. Present the literature and describe the statistical methods and the corresponding literature, as the case demands.

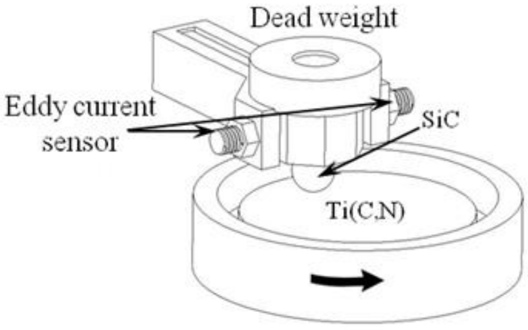

Fig.2 The scheme of experimental apparatus

Test conditions are shown in table 2. Three kinds of the lubricants: purified water, artificial seawater and NaCl solutions with different concentrations are used in this work. Table 3 gives the composition of the seawater, which was prepared according to ASTM D1141-98. Before each test, specimens were cleaned with ethanol and purified water in an ultrasonic bath for 5 min, respectively.

Table 2. Test conditions

Sliding speeds (mm/s)	100, 200
Normal loads (N)	5
Time (min)	2160, 3160
Temperature (oC)	20
Lubricants	Purified water, seawater and NaCl solutions

Table 3. Chemical composition of seawater

Compound	Concentration（g/L）
NaCl	24.53
MgCl2	5.2
Na2SO4	4.09
CaCl2	1.16
KCl	0.695
NaHCO3	0.201
KBr	0.101
H3BO3	0.027
SrCl2	0.025
NaF	0.003

After friction tests, the worn surface micro morphologies were observed by scanning electron microscopy (Hitachi SU8010, Japan) and a surface mapping microscope (Rtec instruments, USA). The chemical elements of wear particles on wear scar were detected by energy dispersive spectrometry. The morphology of wear particles dispersed in the collected lubricant after running-in were obtained using bright field transmission electron microscope (JEM-200CX, Japan), with sample prepared by evaporating dilute suspension on carbon-coated copper films.

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3 RESULTS AND DISCUSSION

Figure 3a shows the friction coefficients of Ti(C,N)/SiC tribo-pair as a function of sliding time in purified water. For the two speed conditions, the starting friction coefficients varied between 0.14 and 0.25 values. After running-in for 1080 min, the coefficient goes into a steady-state value of about 0.2 for the high speed of 200 mm/s condition. While in the case of 100 mm/s, the coefficients exhibit a large fluctuation without steady values. Further, the final friction coefficient is a little higher than those of the high speed condition. It indicated that the two friction behaviors are both in the boundary lubrication regime according to the corresponding coefficients.

Figure 3b presents the friction coefficients of the tribo-pair as a function of sliding time in seawater. Compared with the purified water lubrication, the coefficients of the two speed conditions decline both, especially for the high sliding speed. Though the changing trend of the coefficients for the low speed is similar to those of purified water lubrication condition, the final steady friction coefficient drops obvious. While in the case of 200 mm/s, a very pronounced running-in period was observed. The friction coefficient reaches about 0.14 for the first 600 min, and then it decreases gradually, finally attains steady-state values of about 0.025. The results mean that the lubrication mechanism changes with sliding speeds and the lower friction coefficients are easier to be established at the higher speed.

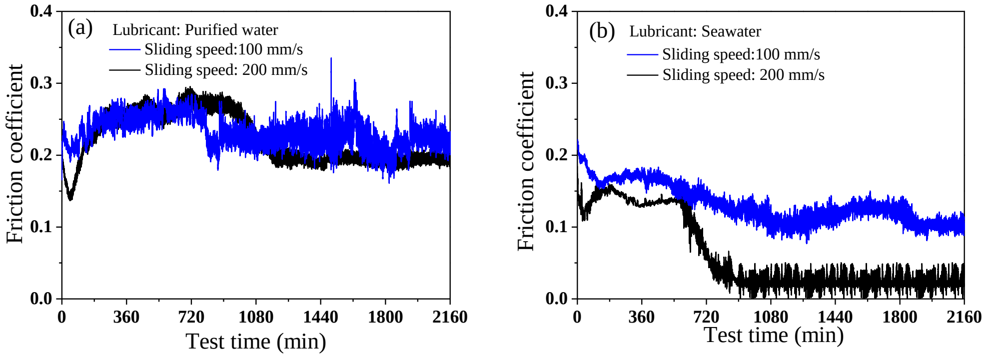

Fig.3 The variation of friction curve at the normal load of 5 N

Figure 4 shows the three-dimensional and sectional morphologies of wear tracks on Ti(C,N) surface at sliding speed of 200 mm/s in purified water and seawater, respectively. The wear width of the two tracks is approximately the same size. However, in purified water, the rough worn surface was observed and the wear track became deeper. When lubricated in seawater, the worn surface became shallow and smooth.

In order to know the wear surface in detail, the SEM images of both the wear tracks and scars were taken. As can be seen in Fig.5a and b, the worn surfaces of the track are relatively rough and there are many irregular convex and cavities distributing in the sliding direction. The observed high friction is probably associated with the cavities and roughness. It can be deduced that, when lubricated with purified water, the wear mechanism may be primarily mechanical wear at the normal load of 5 N. While in the seawater case, two typical worn surfaces are observed. Fig.5c presents the SEM image of the low sliding speed condition and very rough surface morphology is found in the wear tracks, which is similar to those of purified water lubricated surfaces. However, in the higher speed of 200 mm/s, the worn surface (see Fig.5d) displays very smooth and flat beside some shallow and fine cavities.

ISSN 2179-3956

According to the above surface analysis of worn tracks, it can be concluded that the smooth and flat worn surface is conducive to achieve low friction. For Si3N4/Si3N4 tribo-pair, Tomizawa and Fischer[2] also observed extremely smooth wear surfaces and suggested the low friction was attributed to hydrodynamic lubrication after an ultra smooth surface was obtained by tribochemical wear.

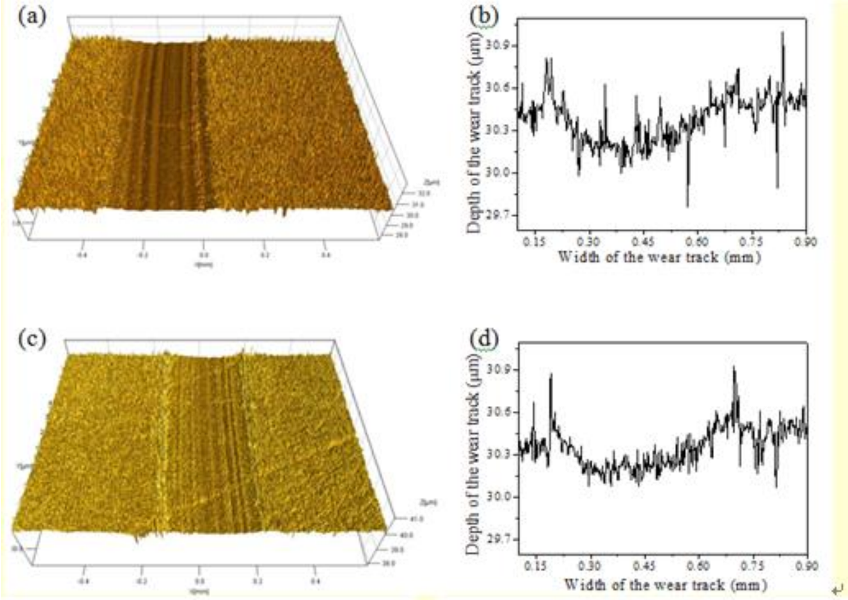

Fig.4 Three-dimensional and sectional morphologies of wear tracks on Ti(C,N). (a) and (b) purified water; (c) and (d) seawater

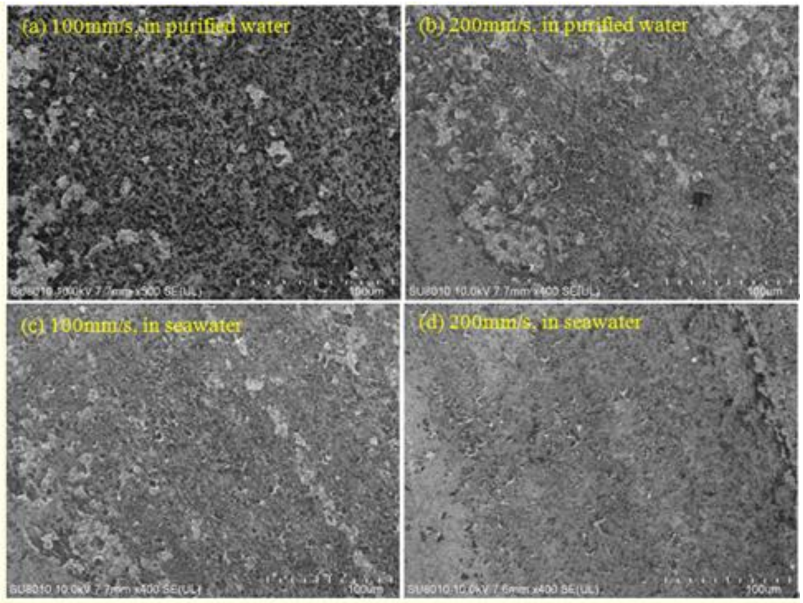

Fig.5 SEM images of wear tracks on Ti(C,N) disks after sliding against SiC for 36 h in various conditions

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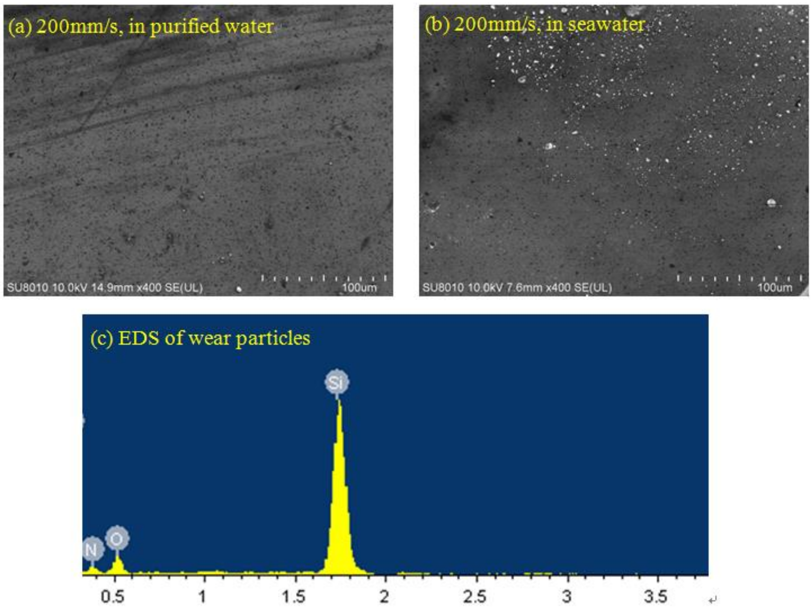

Fig.6 SEM images of wear scar on SiC balls after sliding against Ti(C,N) for 36 h in various conditions (a and b), (c) EDS of wear particles on wear scar in seawater

Figure 6 presents the SEM images of wear scar on SiC balls after sliding against Ti(C,N) for 36 h in high speed conditions. The worn surface of the ball in purified water was covered with many shallow scratch grooves along the sliding direction. In addition, a large fracture pits or voids were observed on the wear scar. For the seawater, the wear scar of the ball exhibited more smooth and flat. More important, many wear particles, with a few microns in size, distributed evenly throughout the wear surface. The EDS analysis of the particles (see Fig.6c) indicates the presence of a strong Si peak coupled with O and N. According to atom stoichiometric ratio, the main component of the particles could be SiO2, which is produced by tribochemical reaction as mentioned in ref.[2, 8, 12]. The products of silica will further hydrate to form silica colloid particles[7]. The tribochemical reactions occurring on the rubbing surfaces of SiC in purified or sea water can be summarized as follows:

$$SiC + 2H_2O \rightarrow SiO_2 + CH_4 \quad \text{Eq.1}$$

$$SiO_2 + 2H_2O \rightarrow Si(OH)_4 \quad \text{Eq.2}$$

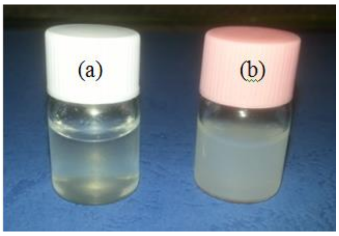

Fig.7 The image of lubricant after 36 h running-in process (a) purified water worked at 200 mm/s; (b) seawater worked at 200 mm/s

Figure 7 shows the lubricants collected after 36 h running-in process at high speed of 200 mm/s. It can be seen clearly that colloidal silica with different concentrations were formed in water and seawater, respectively. As pointed in ref.[20], silica carries a net negative charge when the pH is above 3.5 and the surrounding ions of seawater will decrease the repulsion effect between the charged silica by neutralizing its bearing charge and accelerate the coagulation. Thus, the silica colloid particles

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will agglomerate and precipitate out continuously, and this could be the reason of forming high concentrated silica colloid in seawater (see Fig.7b).

Figure 8 presents the TEM images and electron diffraction patterns of the particles in the two kinds of lubricants (shown in Fig.7). Fig.8a shows the sheet wear particles with the sizes of several tens to a hundred nanometers. The agglomerate phenomenon is not serious for the low particle concentration. The electron diffraction pattern suggests that the silica colloid particles are fine crystalline (see Fig.8b). While in seawater, there exists severe agglomerate of needle-like particles whose size is smaller than those formed in purified water (see Fig.8c). The agglomerate phenomena may result from the existing of salt ions. The electron diffraction pattern reveals that the colloid particles are amorphous (see Fig.8d).

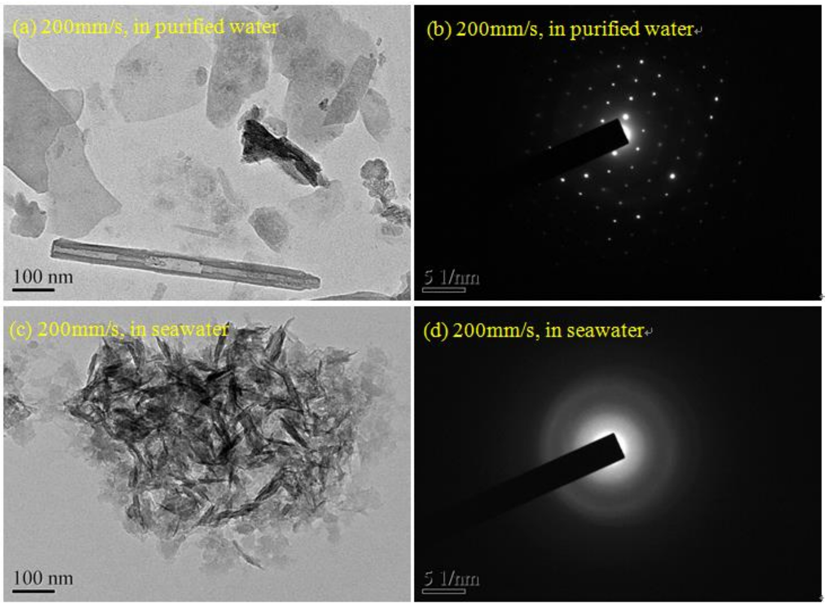

Fig.8 TEM images and electron diffraction pattern of colloid particles formed in various conditions. (a) TEM image of particles in Fig.7a; (b) Electron diffraction pattern of particles in Fig.7a; (c) TEM image of particles in Fig.7b; (d) Electron diffraction pattern of particles in Fig.7b

Compared with purified water, high content of silica in seawater can serve as effective lubrication layer, which may contribute to achieve low friction coefficient. Besides, the viscosity of the lubricant formed in seawater is much higher than that of in purified water. The higher of colloidal viscosity it is, the easier of inducing hydrodynamic lubrication will be. In the case of seawater lubrication, both the mechanical and tribochemical wear happened on the interface of Ti(C,N)/SiC tribo-pair. With the increase of sliding speed from 100 to 200 mm/s, the lubrication mechanism may change from boundary lubrication to mixed or partially hydrodynamic lubrication.

To further identify the role of silica colloid during the lubrication process, the friction test of Ti(C,N)/SiC tribo-pair in seawater followed by purified water was carried out and the friction coefficients as a function of sliding time was shown in Fig.9. After running-in for about 1800 min in seawater, the tribo-pair exhibits a low friction coefficient of 0.02. According to the analysis mentioned above, it is believed that both the smooth rubbing surface and silica colloid with a certain concentration have been formed. At the moment of 2340 min, silica colloid was moved from the container and purified water was added. Significant increase of coefficient from 0.02 to 0.15

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appeared. It can be deduced that flat surface is not the only condition necessary for low friction and high concentrated silica colloid is also an essential one.

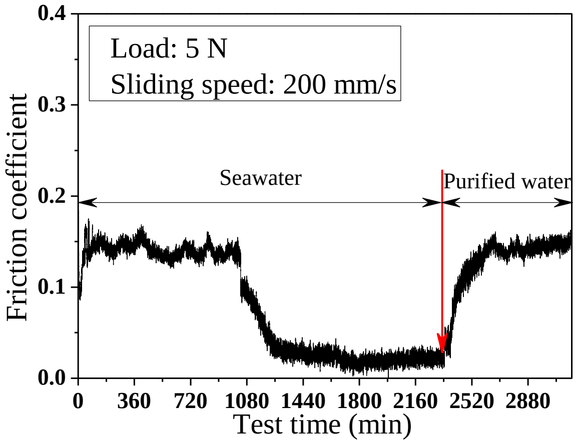

Fig.9 The friction test of Ti(C,N)/SiC tribo-pair in seawater followed by purified water

As can be seen, the silica colloid acts as one of the crucial factors, which contribute to the low coefficient under seawater lubrication. However, it is unclear that under which salt ion concentration can effective silica colloid be formed during the friction process. To simply clarify the influence of ion concentration, a series of friction test of Ti(C,N)/SiC under the lubrication of NaCl solutions with different concentrations were performed, since the main composition of the seawater is NaCl.

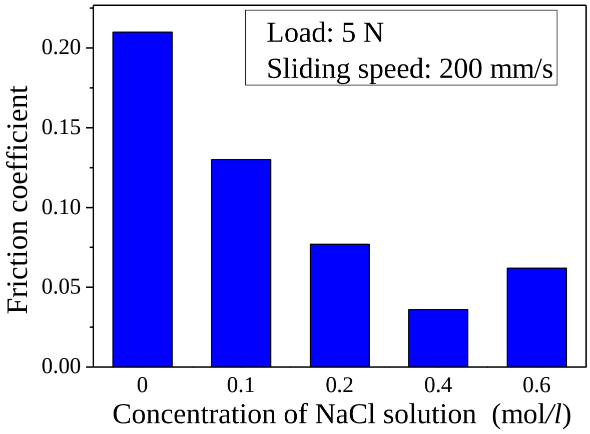

Fig.10 The relation between the NaCl concentrations and friction coefficients

Figure 10 presents the relation between the concentration of NaCl solution and the stable friction coefficient, which was averaged from the recorded data of the 36th hour. It is clear that the friction coefficient of Ti(C,N)/SiC tribo-pair in purified water (0 mol/l) is higher than those in NaCl solutions. When lubricated with NaCl solutions, the coefficients first decrease from 0.13 to 0.036 with the increase of ion concentrations and then increased gradually to the value of about 0.062 at the corresponding concentration of 0.6 mol/l.

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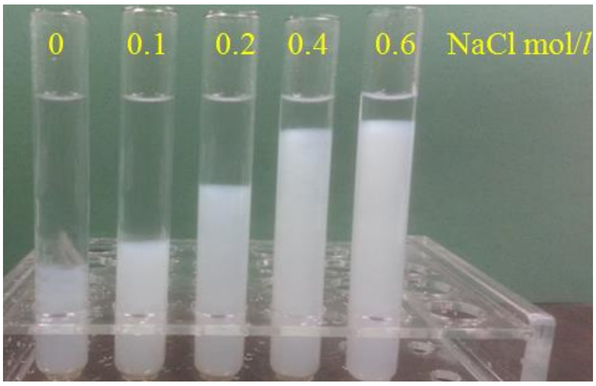

Fig.11 Five lubricants collected after 36 h friction test and let them sit for 12 h

The lubricants collected after 36 h running-in process at different salt concentrations and let them sit for 12 h were shown in Fig.11. As can be seen, there exists obvious stratification of the water and colloidal particles, and only a very small amount of silica colloid formed in the purified water lubrication condition. While in the case of NaCl solution lubrication, a certain concentration of silica colloid is formed during the friction course and the content increases with the increasing of ion concentration in general. As mentioned above, the colloidal particles tend to aggregate and precipitate out due to the presence of ions, which will accelerate SiC hydrolysis (Eq.1) and SiO2 hydration (Eq.2) reactions. As reported in ref.[6], the colloidal silica adsorbed on the friction surface could act as a lubricant layer to recover the locally worn out films. It shows that the higher concentration of colloidal particles, the lower friction coefficient it remains. The increasing coefficient at the NaCl molar of 0.6 mol/l could result from the excessive particles content.

4 CONCLUSION

In this paper, the tribological behavior of Ti(C,N) sliding against SiC ball in water and seawater were evaluated in detail by a ball-on-disk tribometer. The normal load is fixed at 5 N and sliding speeds are 100 and 200 mm/s. The main results can be summarized as:
(1) When lubricated in purified water, the friction coefficient is about 0.2, while in seawater, the friction coefficient decreases dramatically from the value of 0.14 to 0.025.
(2) In seawater, high speed of running-in process helps to nurture smooth and flat surface, which is one of the essential conditions for low friction.
(3) Salt ion molar in water plays a key role in forming concentrated silica colloid and proper concentration of colloidal particles in lubricant is contributed to achieve low friction coefficient.

Acknowledgments

This research is supported by A Project Funded by Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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