

Influence of electric potentials on the tribological behaviour of silicon carbide

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Abstract

Thanks to their superior friction and wear properties in aqueous environments, silicon carbide (SiC) ceramics are commonly used for slide bearings and face seals in pumps. Tribochemical reactions of SiC with water have a major influence on the frictional behaviour as well as on the wear rates. It has been presumed that low friction coefficients (in the order of 0.1) are reached by smoothening of the surfaces, which favours hydrodynamic conditions even in water, and by the formation of lubricious oxide scales through tribochemical reaction of SiC with water.

Silicon carbide is electrically semiconducting. Due to additives like boron or aluminium, silicon carbide ceramics can exhibit a considerable specific electrical conductivity. Therefore, electrochemical reactions with water or aqueous electrolytes and subsequent friction, wear and corrosion may be influenced electrochemically. A pin-on-disc tester was modified to study SiC under the influence of electric potentials between -1 and +1 V (vs. Ag/AgCl). It was observed that under cathodic polarisation of the SiC samples, both friction coefficient and wear rates were drastically decreased. Surprisingly, despite the formation of oxide scales under positive (anodic) polarisation the friction coefficients increased significantly, which contradicts the fundamental hypothesis of a lubricating effect of the oxide scales. After switching off the electric potentials, the friction coefficient instantly changed to adopt normal values of ca. 0.1. These results show that it is possible to influence or even control the tribological behaviour of electrically conductive ceramics in aqueous media by electric potentials. New models based on electrochemical surface effects are necessary to describe the observed effects.

Keywords: Silicon carbide, SiC, water, friction, wear, electric potentials

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Nomenclature

CE	counter electrode
COF	coefficient of friction
E_{corr}	corrosion potential
FESEM	field emission scanning electron microscopy
ICP-OES	inductive Coupled Plasma-Spectroscopy
i_{corr}	corrosion current density
LSV	linear scan voltammetry
ocp	open circuit potential
RE	reference electrode
SCE	saturated calomel electrode
WE	working electrode
ζ	zeta potential

1. Introduction

In pumps and compressors, ceramic slide bearings and face seals play an important role [1,2]. Though they are only lubricated by the transported media, which are mostly aqueous and sometimes chemically aggressive, they must work under mixed lubrication conditions in a very stable and reliable manner. Silicon carbide has been established as a high performance material for sliding bearings and seals: it is very resistant against corrosion and wear and yields low friction coefficients under mixed water lubrication conditions. However, there are some technical applications, in which ceramic parts still cause problems, because the frictional behaviour may rise instantly and become unstable due to lack of water between the sliding contacts. Some chemically aggressive media and also pure deionized water may also cause premature failure of the ceramic components because of very high wear and even active corrosion. Considering the very high requirements concerning reliability and lifetime in chemical and power plants, there is a clear need to further improve the corrosion and wear properties of silicon carbide ceramics or to develop wear and corrosion protection techniques.

Water lubricated ceramic friction contacts are very stable as long as tribochemical reactions of water with the interacting surfaces occur. These chemical reactions may lead to the formation of superlubricious phases i.e. to tribological regimes with nearly zero friction [3,4]. On the laboratory scale, very low friction and wear conditions were obtained, especially with silicon carbide and nitride based ceramics. The fundamental friction and wear mechanisms have been studied extensively but they are not yet completely understood because of their complexity. The following relevant mechanisms have been discussed:

- Tribochemical reactions [5,6]: Within the sliding contacts, mechanical and thermal stresses induce an accelerated chemical reactivity and therefore to the chemical reaction of SiC with water. These tribochemical

reactions cause mild wear conditions and therefore, the removal of surface asperities, which favours hydrodynamic lubrication even at very low lubricant viscosity.

- The SiO₂-based reaction products contain considerable amounts of water, since SiO₂ reacts with water to form silicon hydroxides. These gel-like silica phases are considered to have a lubricious effect and therefore strongly reduce friction [7].
- Less known are the publications of Cheng et al. [8] and Zhang et al. [9] who proposed a lubricous effect of the electrochemical double layer at the SiC-water interface. Since the diffuse part of this layer gets sheared in the sliding contact, electrical charges are moved. These may cause an increase of the viscosity at the interface, which may affect friction and wear of ceramic surfaces at very thin lubricant films [10,11].

Due to their electrical conductivity, the friction and wear behaviour of silicon carbide based materials may be influenced by electric potentials applied to the tribological system. Although there exist only a few publications on the influence of electrical potentials on the tribological behaviour of steel-ceramic sliding pairs [12, 13] and steel in contact with hard coatings (e.g. TiN-coatings [14]), there have been some observations in technical systems that clearly show an influence of electric potentials on the tribological and corrosion damage behaviour of ceramic components [15]. Also, electrochemical corrosion studies [16,17] and studies on electrochemical etching [18] show that the surface state of SiC ceramics can be influenced by electrical potentials. The complex interplay between mechanical, chemical, and electrochemical interactions during tribo-corrosion was recently discussed by J.-P. Celis et al. [19]. The work shows the possibility to investigate in-situ electrochemical (corrosion) and mechanical (friction and wear) interactions at the surfaces, which are immersed in electrolytes like water-based solutions.

An electrochemical characterisation of solid state sintered silicon carbide ceramics is given in ref 17. In this paper it was demonstrated that for SSiC ceramics with specific electrical resistivity of 2.5 Ωm surface scales of amorphous silicon dioxide could be produced by anodic oxidation at elevated potentials (2 V) in acidic media. In alkaline media anisotropic electrochemical etching of the SSiC-ceramic was observed. This is in accordance with the potential—pH equilibrium diagram for the system silicon—water [20]. Above a pH-value of 10 soluble silicates are the predominant species.

So far, despite the very large technological impact, neither the materials development nor the electrochemical approaches have yet been examined. In addition, the fundamental understanding of the tribological behaviour of silicon-based ceramics in water environment is only fragmentary.

The aim of the present work was therefore to carry out a fundamental study of the influence of electric potentials on the friction, wear and corrosion behaviour of silicon carbide in water and to find out if electrochemical techniques may be applied as wear and corrosion protection measures. For this study a pin-on-disc tribometer was modified in order to apply electric potentials during a friction and wear test. Complementary electrochemical corrosion studies were performed to study the effect of electric potentials on chemical reactions with water. The findings of this experimental work is analysed and discussed taking electrochemical effects into consideration to explain the tribological results.

2. Experimental

For the tribological studies, a standard pin-on-disc setup (TRM 1000, Wazau, Germany) was used, in which the pin specimen is fixed within a lubrication pot (fig. 1). The load is applied by dead weights that press the lower test setup against a rotating disc. For the electrotribological studies, sample holders and electrolyte container were made of PMMA to realise an electrically isolating environment. Electrodes were applied as shown in fig.1: A platinum electrode was used as the counter electrode (CE) and a standard Ag/AgCl-electrode as the reference electrode (RE). The fixed pin was electrically contacted at its backside and defined as the working electrode (WE). Potential difference control between RE and WE, and measurement of the current between CE and WE was conducted using a potentiostat (Wenking LPG03-50, Bank Elektronik GmbH, Pohlheim, Germany).

Materials and samples

The silicon carbide used throughout this work was a commercially available material (EKasic D®, ESK Ceramics, Kempten, Germany). This material is a solid state sintered silicon carbide (density: 3.16 g/cm^3) containing minor amounts ($<1\text{wt.}\%$) of aluminium as sintering aids ($< 98\%$). The grains are platelet like with grain sizes up to 20- 40 μm . Ekasic D was chosen because of its good electric conductivity ($2.5 \Omega\text{m}$) and therefore good response to electric potentials. The investigations in a second step will be expanded to SiC materials with lower conductivity. The discs had a quadratic shape (40 x 40 mm, thickness: 5 mm) with a surface roughness of $R_a: 0.06 \mu\text{m}$ and $R_z: 0.41 \mu\text{m}$. The pins were also cut from quadratic rods (8 x 8 mm, length: 10 mm), the contact site of the pin was ground to a spherical shape (radius: 10 mm). The pin has an initial surface roughness of $R_a: 0.15 \mu\text{m}$ and $R_z: 0.84 \mu\text{m}$.

Test conditions

The test conditions, at which tribological experiments were performed, are summarized in table 1. These parameters were selected to study the principal influence of electrolyte composition (pH and concentration and type of ions). Of course, more complete series of parameters should be used in future studies, but to show the principal effects, these parameters are sufficient. Precise specifications of test conditions are given in the figure captions of each diagram in the results section.

3. Results and interpretation

Electrochemical behavior of SiC

Results of linear sweep voltammetry (LSV) for SSiC in 0.5 M H₂SO₄ are shown in fig. 2a. The scans have been recorded with a scan rate of $dE/dt = 0.5$ mV/s in a potential range from -0.6 V up to 0.8 V versus SCE, that is before cathodic hydrogen evolution and prior to anodic oxygen evolution. The detailed analysis clearly showed that in the anodic part of the LSV, in acids and neutral solutions a SiO₂ passive layer is formed [16, 17]. Fig.2b shows a long term exposure of the SiC in acidic solution. At begin of the exposure the open circuit potential (ocp) is in the same range as the E_{corr} measured by LSV under the same condition (fig.2a). However, the ocp rises up to 0.3V_{SCE} over the the time of exposure. This value is equivalent to the potential of the active-passive transition shown in Fig.2a and is caused by the formation and growth of the passive SiO₂ layer. The occasional potential drops can be explained by internal stress induced cracks and immediate re-passivation.

Influence of electric fields on friction

In fig. 3, a first potential scan of the corrosion current and the corresponding friction coefficient during a running tribological test is shown. Starting at a potential of -300 mV, the voltage was increased to -20 mV within 10 min. The potential, current and the corresponding friction coefficient were measured. Due to the variable contact conditions in the sliding contact, there is a significant scatter of the electrical signals, but the typical shape of a potential curve is clearly visible. Furthermore because of this variable contact conditions fig. 3 shows the corrosion current and not the corrosion current density.

The most interesting observation shown in this diagram is the potential dependent course of the friction coefficient (COF). At cathodic potentials (< 220 mV), the COF was decreased to values as low as 0.02. A transition to enhanced COF was observed, when the potential was shifted to anodic conditions (> -200 mV). Finally an abrupt change of the COF to mean values of ca. 0.1 appeared, when the potentiostat was turned off.

To study the effect of electric potentials on friction three potentials were selected, at which tribological tests were conducted under constant conditions (fig. 4). At +300 mV, the observed COF remained constant at ca. 0.17. At a potential of -216.5 mV, which corresponds to the corrosion potential (s. fig 3), the COF was slightly below 0.1. This COF was also observed in the absence of electric potentials. The lowest COF was observed with cathodic potentials (-300 mV). In each test, there occurred a sudden change of the COF to 0.1, when the voltage supply was switched off.

This result already shows that there is a clear dependence of the friction coefficient on the applied electric field. Surprisingly however, the lower friction coefficient was not observed under anodic conditions, at which oxidation of silicon carbide takes place. The only electrochemical reaction that can be expected at -300 mV is the reduction of oxygen to form OH⁻ and therefore may cause a slight surface-near pH increase. Although this may imply that a tribofilm may form on the surface under these conditions, the extremely low wear rates, which were also measured, contradict the hypothesis of the occurrence of any chemical reactions to form soft tribofilms because they would be easily worn off. In addition, the abrupt changes of the COF after turning off the potential cannot yet be explained, since a relaxation of the electrochemical potential generally takes a certain time. It is also clear that chemical reactions that may be triggered by electric potentials are too slow to cause abrupt changes of

the friction coefficient. In contrast, the double layer models [8-10] seem more likely since these respond very quickly to potential changes.

The FESEM analysis of the worn surface showed no SiO₂ layer formation even under conditions, where an electrochemical formation of the SiO₂ layer due to SiC oxidation is expected [16, 17]. This indicates that the formed SiO₂ is directly removed by the wear due to sliding contact.

Regarding the friction mechanisms described in section 1, this observation cannot be explained by the hypothesis of a lubricious effect of silicon oxides formed in the sliding contact which has been postulated by Xu [7] and many others. In contrast, the hypothesis that the electrical double layer is supporting and stabilising hydrodynamic lubrication seems more adequate. At cathodic polarisation, cations are attracted to the SiC surface. Therefore, within the electric double layer, these cations may play a decisive role concerning the near-surface viscosity. Little is known about electrokinetic effects at electrified surfaces in concentrated electrolytes [21], but it is undoubted that the electric double layer is influenced in the presence of electrical potentials. At high shear rates occurring in very thin lubricant films, charge movement in the diffuse layer causes a significant increase of the viscosity, which in consequence stabilises hydrodynamic conditions.

This consideration implies that the nature and concentration of cations in the electrolyte should have an influence on the tribological behaviour of electrically polarised ceramic surfaces. Therefore, the NaCl solution was replaced by KCl and HCl to check if the change of the cation affects friction and wear. Results of these studies are shown in fig. 5a. In fig 5b the corresponding currents are shown. It can be seen that during the whole experiment the currents were negative, which indicates that the polarisation of the sliding pair was cathodic. Current changes that were measured when NaCl and KCl were used as electrolytes do not directly correlate with the COF and may rather be assigned to reduction of oxygen, which was probably dissolved in the electrolyte.

Repeated tests at cathodic polarisation using NaCl and HCl yielded COFs that are clearly lower than the COF observed with unpolarized surfaces. When KCl was used, the decrease of the COF was also significant but the friction level was higher than in the case of NaCl- and HCl-solutions.

Influence of electric fields on wear

After the tribological experiments, wear was measured using stylus profilometry. In fig. 6 profiles of wear scars of a series of pin-on-disc tests are plotted. Wear scars are visible after tests without electric potential, at anodic potentials (+300 mV) and at the corrosion potential (-216.5 mV). Only a slight reduction of the surface roughness is visible after tests at cathodic potential (-300 mV).

Wear volumes were determined from the wear profiles. The overview in fig. 7 clearly shows that under cathodic potentials, the wear is strongly reduced.

Due to the very small wear rates, the linear wear is not measurable by monitoring the height change. Since the wear of SiC in water is chemical, there is an increase of concentration of dissolved silica in the electrolyte. To measure the chemical wear, small amounts of electrolyte were continuously taken and analysed using inductive coupled plasma-spectroscopy (ICP-OES). This method, which is described in more detail in a separate paper [22],

allows an accurate measurement of low silica concentrations in aqueous media even in the presence of high concentrations of other dissolved salts.

In fig. 8, the time-dependent wear of SiC in NaCl solutions is shown. Surprisingly, the wear rate was significantly lower in higher concentrated NaCl-solution. This observation may be explained by the lower solubility of silica and Na-silicates in highly concentrated solutions [23]. In previous studies on the sliding friction and wear behaviour of SiC in acids and bases [24], the nature of the solution was reported to have a minor effect on wear. However, in that study, the solutions were clearly less concentrated than the NaCl solutions used in the present study. Actually, we have not found any published work, in which the tribological behaviour of SiC in NaCl solutions has been studied in detail.

The influence of electric potentials on wear behaviour of SiC is shown in fig. 9. By monitoring the silica concentration in the water, it is clearly observed that wear was significantly lower when cathodic potentials were applied. The friction coefficients of these experiments are shown in fig. 5. It was even observed that the silica concentration became constant after a short running-in period, which means that the wear rates were decreased to nearly zero.

Discussion

The results show that there is a clear influence of electrical potentials on friction and wear of silicon carbide in water. Not only friction coefficients are strongly decreased but also the wear rate is minimised in the presence of cathodic surface potentials in the range of ca. 100 mV below the corrosion potential. Regarding the earlier work on tribological behaviour of SiC in aqueous media [4-8,24], it is clear that surface chemical effects play an important role. However, chemical reactions that lead to the formation of silica [7] cannot be the only and essential mechanism which leads to low friction, since the lowest friction coefficients were observed at surface potentials at which a chemical reaction of SiC should not take place at all. Electrochemical corrosion experiments [17], evidently show that oxidation of SiC and the formation of silica takes place at elevated anodic potentials. The results of the additional wear monitoring test using ICP analysis also show that a continuous formation of silica is not necessary for the stabilisation of low friction.

On the other hand, the hypothesis of Chen and Zhang [8,9] as well as Prive et al. [10], who proposed that electrokinetic phenomena within the electric double layer influence the frictional behaviour, seems to be valid.

In neutral electrolyte concentration the used SiC has a negative ζ potential. The cathodic polarisation of the ceramic surface therefore leads to a modification of the electric double layer and probably increases the near-surface charge density or the DL thickness (Fig. 10). By shearing the diffuse part of the double layer, the motion of electric charges causes a significant increase of the near-surface viscosity. Enhanced viscosity at the surfaces stabilises the friction at a low level, because solid-solid contacts are prevented. The influence of the cathodic polarization on electric double layer therefore acts as an efficient buffer under mixed lubrication conditions (fig. 11). Consequently, in the absence of solid-solid contacts as well as tribochemical reactions the wear rates become extremely small.

Conclusions

In pin-on-disc experiments, the tribological behaviour of sintered SiC was significantly influenced by electric potentials, when highly concentrated electrolytes (NaCl, KCl, HCl, 1 mol/l) were used as lubricants. Under cathodic polarisation of the SiC samples, both friction coefficient and wear rate were drastically decreased. Anodic polarisation of the sliding samples resulted in enhanced friction coefficients and corrosive wear. These results demonstrate a beneficial effect of electric potentials of friction, corrosion and wear by influencing the electrochemical interactions at the ceramic surfaces.

The mechanisms leading to this effect are not yet understood, but it is supposed that electrokinetic effects induced by shearing the electric double layers cause enhanced surface near viscosity and therefore stabilise hydrodynamic lubrication conditions. Under cathodic polarisation of the sample surface, the surface electrochemical reactions of SiC with water are diminished significantly thus chemical wear rates become extremely low.

Since SiC components are commonly used as slide bearings and seals in aqueous media, it is supposed, that friction, wear and corrosion of these components may also be reduced by applying electric potentials.

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