TRIBOLOGICAL INTERACTIONS BETWEEN SINGLE-CRYSTAL DIAMOND AND THERMALLY OXIDIZED SINGLE-CRYSTAL SILICON CARBIDE ON MICROSCALE

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SUMMARY
The microtribological behaviour of diamond/silicon carbide sliding pairs in unlubricated, reciprocating sliding contact was measured experimentally using a modified atomic force/friction force microscope (AFM/FFM). Untreated and thermally oxidized, commercial single-crystal 6H-SiC ceramics were mated to a natural single-crystal diamond tip. As reference, Si(111) and amorphous SiO2 samples were tested under equal conditions. Nanoindentation techniques as well as Auger electron spectroscopy were used to characterize various compound layers present on the sliding surfaces before and after the microtribological tests. Friction and wear mechanisms are discussed as function of surface composition resulting from different thermal preoxidation treatment.

Keywords: Silicon carbide, diamond, atomic force microscopy, sliding wear, microtribology

1 INTRODUCTION
Advanced silicon carbide (SiC) ceramics show a tremendous potential for the industrial applications as mechanical face seals or journal bearings in pumps, as heating conductors and burning nozzles. Micromechanical and microelectromechanical (MEMS) devices, e. g. micromotors and reading/writing heads in computer hard disks, are other fields of increasing interest for using these ceramic materials owing to increasing tendency for miniaturisation [1]. Silicon carbide ceramics offer a great potential for tribological, chemical and/or thermal high duty components, because of their low density, high hardness, chemical inertness, oxidation resistance and thermal stability as well as high thermal conductivity. Tribological behaviour of these materials is influenced by oxidation reactions at the presence of oxygen and/or humidity in surrounding atmosphere and by hydrooxidation reactions under conditions of boundary lubrication in water [2-4]. Thereby, the composition and properties of the oxide layers of the SiC surfaces are of highly practical interest. Studies of the microtribological behaviour of a single-crystal natural diamond tip sliding on silicon without any oxide layer (HF etched) as well as with a native oxide layer or a dry-oxidized SiO2-coating using AFM showed distinct differences in friction coefficient and amount of linear wear [5].

The aim of the present study was to identify the factors affecting the tribological behaviour of untreated and thermally oxidized SiC/diamond sliding pairs in unlubricated contact at very low sliding speed in ambient air. The tribological tests were conducted using a diamond tip in a modified atomic force/friction force microscope and were supplemented by studies using Auger electron spectroscopy as well as nanoindentation techniques.

2 TEST SPECIMENS AND EXPERIMENTAL METHODS
The test specimens used in this study (Table 1) were untreated and thermally oxidized single-crystal 6H-SiC wafers (Cree Research Inc., Durham, NC) with orientations in the directions (0001) ± 0.5 degree and (0001) ± 0.5 degree, respectively. The ideal 6H-SiC crystal structure (Fig. 1) possesses a crystallographic polarity in the {0001} orientations due to the silicon and carbon heteroatoms [6]. For 6H-SiC the ideal (0001) basal surface is terminated by silicon atoms (SiC-Si0), whereas the ideal (0001) basal surface is terminated by carbon atoms (SiC-C0). Thermal oxidation treatments were carried out on SiC-Si0 samples in an alumina tube furnace under flowing synthetic air (dry and free of oil) at temperatures of 625°C or 1050°C (Table 1). In addition, a single-crystal Si(111) wafer and an amorphous SiO2 sample were used as reference. The surface roughness of the SiC-samples increased only slightly from a mean R_a value of 0.40 nm (measured by AFM over a scan range of 10 x 10 µm^2) for untreated SiC-Si0 and SiC-C0 to 0.45 nm and 0.50 nm after thermal oxidation for SiC-Si6 and the various SiC-Si10 samples, respectively. Si(111) and a-SiO2 showed smaller mean values of surface roughness R_a of about 0.10 nm and 0.20 nm, respectively.

Surface topographies as well as nanohardness measurements and microtribological experiments were carried out using a modified atomic force/friction force microscope (AFM/FFM, model Discoverer, TopoMetrix, Santa Clara, CA). The indentor used for hardness measurements was a three-sided equilateral pyramidal natural diamond tip with included apex angles of 60° and a tip radius of 15 nm (see SEM micrograph in Fig. 2) mounted on a platinum coated stainless steel cantilever beam (Olympus Optical Co., Japan) with a bending stiffness (spring constant) of 1500 N/m. The microtribological behaviour of the various SiC samples was measured in unlubricated, reciprocating sliding contact to the diamond tip using values of the bending stiffness of 2.2 or 50 N/m and parallel mode, i. e. the scan direction was parallel to the long axis of the cantilever (Fig. 2). During forward motion one of the three edges of the diamond tip was leading whereas during backward motion it trailed. The normal force was 60 µN, the slid-
ing speed 10 µm/s, the stroke 5 µm and the total length of sliding path added up to 2 mm, consisting of 200 parallel, reciprocating scan lines with an offset of 25 nm between two neighbouring lines. During the tests, friction coefficient was measured whereas the amount of linear wear was determined from the resulting surface topography. All tests were carried out in synthetic air (dry and free of oil) at room temperature under controlled relative humidity of 30% in a climate chamber. Before the tests, the specimens were cleaned with isopropanol for 15 min using an ultrasonic bath. In addition, the chemical composition of the various specimens was analysed using Auger electron spectroscopic (AES) depth profiles before and after the tribological tests.

3 RESULTS

Fig. 3 displays the oxide layer thickness of the various samples calculated from AES depth profiles. The untreated SiC-Si0 and SiC-C0 samples showed 1.0 ± 0.5 nm thick native oxide layers. With increasing oxidation temperature and exposure time the oxide thickness increased in the order of SiC-Si0 (1.0 ± 0.5 nm), SiC-Si6 (1.5 ± 0.5 nm), SiC-Si10 or SiC-Si10H (2.5 ± 0.5 nm), SiC-Si10h3/4 (8.0 ± 1.5 nm) and SiC-Si10h10 (38 ± 5 nm), respectively. Nanohardness values were measured on the various samples using the normal force of 100 µN. The highest values of nanohardness were determined on untreated SiC-Si0 and SiC-C0 with 29.3 and 26.1 GPa, respectively. With increasing oxidation temperature and increasing exposure time at 1050°C the values of nanohardness decreased distinctly in the order of SiC-Si0 (29.3 GPa), SiC-Si6 (24.2 GPa), SiC-Si10 or SiC-Si10H (21.6 GPa) and SiC-Si10h10 (11.5 GPa).

Before the tribological experiments a running-in procedure was performed on the diamond tip by sliding it on SiC-Si0 for about 50 mm at the operation conditions (Fig. 2). This procedure resulted in a distinct change of the geometry of the diamond tip as can be seen by comparing Fig. 2 (tip radius 15 nm) and Fig. 4 (tip radius about 145 nm). After performing the running-in procedure, a further significant change in the geometry of the diamond tip owing to the following tribological tests could not be measured, that was regularly checked by measuring the topography of the diamond tip using AFM.

<table>
<thead>
<tr>
<th>Thermal treatment</th>
<th>Specimens</th>
<th>Si(111)</th>
<th>Amorphous SiO₂</th>
</tr>
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<tbody>
<tr>
<td>Untreated</td>
<td>SiC-C0</td>
<td>SiC-Si0</td>
<td>Si(111)</td>
</tr>
<tr>
<td>625 °C / 3 h</td>
<td>SiC-Si6</td>
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<tr>
<td>1050 °C / 0.25 h</td>
<td>SiC-Si10</td>
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<tr>
<td>1050 °C / 0.25 h +</td>
<td>SiC-Si10H</td>
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<tr>
<td>90 °C / 60 h H₂O</td>
<td>SiC-Si10h3/4</td>
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<tr>
<td>1050 °C / 0.75 h</td>
<td>SiC-Si10h10</td>
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<td>1050 °C / 10 h</td>
<td>SiC-Si10h10</td>
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Table 1: Specimens and thermal oxidation treatment used in this study.
Fig. 5 shows exemplary AFM gradient images of the surface topographies of SiC-Si6 and SiC-Si10h3/4 samples after the tribological tests (one reciprocating sliding cycle on each trace) using the diamond tip with a radius of 145 nm. As visible, a surface smoothing occurred during the sliding action of the diamond tip. On the untreated SiC samples and on SiC-Si6 (Fig. 5a) polishing grooves still existed in the worn area, owing to a greater amount of linear wear surface structures and polishing grooves of the original surface disappeared on SiC-Si10h3/4 (Fig. 5b). Wear debris mostly round in shape and with diameters of about 200 nm adhered at the edge of the worn area. Pile ups around the worn area due to plastic deformation were also observed.

The mean values of the amount of linear wear determined from surface topographies after the tribological tests are summarized in Fig. 6a. The lowest values of linear wear were measured on untreated SiC-Si0 and SiC-C0 with 0.8 and 0.6 nm, respectively. With increasing oxidation temperature and exposure time a distinct increase in linear wear in the order of SiC-Si0 (0.8 nm), SiC-Si6 (1.3 nm), SiC-Si10H (2.5 nm), SiC-Si10 (2.6 nm) and SiC-Si10h3/4 (6.9 nm) was observed. The reference samples Si(111) and a-SiO2 showed far greater values of 29 and 27 nm, respectively.

In Fig. 6b the mean values of the friction coefficient are displayed for the various sliding pairs. Sliding pairs with untreated SiC-Si0 and SiC-C0 showed the lowest values of 0.18 and 0.17, respectively. The friction coefficient increased from 0.17 for SiC-Si0 to 0.18 for SiC-Si6 and 0.19 for SiC-Si10. Increasing the oxidation time from 0.25 h (SiC-Si10) to 0.75 h (SiC-Si10h3/4) at 1050°C resulted in an increase of the friction coefficient form 0.19 to 0.23. Only the pairs with the reference samples showed higher values of friction coefficient of 0.31 and 0.30, respectively.

Changes in surface composition induced by the tribological interactions were studied by comparing AES depth profiles before and after the tests. Oxide thickness values of some samples determined from the decrease of the oxygen AES peak signals are presented in Fig. 7. The oxide thickness on Si(111) increased from 1.5 nm to 4.0 nm owing to the tribological interaction. However, a different tendency was observed on SiC samples: while SiC-Si0 showed an increase in oxide thickness from 1.0 to 2.0 nm, thickness on SiC-Si10H decreased from 3.0 to 2.0 nm. In either case, however, oxide thickness after the tribological test was determined to 2.0 ± 0.5 nm, independent of the thickness before the test.

4 DISCUSSION AND CONCLUSIONS

Microtribological tests were carried out to study the tribological behaviour of untreated and thermally oxidized SiC samples in unlubricated, reciprocating sliding contact to a well defined natural diamond tip with a radius of about 145 nm. Various compound layers present on the untreated and oxidized sample surfaces before and after the tribological tests were identified and characterized by nanoindentation techniques using AFM/FFM. With increasing oxidation temperature a slight increase in surface roughness and a more distinct increase in oxide thickness was found (Fig. 3). Nano-hardness values of SiC-Si0 using the normal force of 100 µN on the sharp diamond tip (radius of 15 nm) were about a factor of 3 greater than those of amorphous SiO2, while values of the SiC samples after the oxidation treatment in synthetic air at 1050°C for 0.75h were only slightly higher than those for SiO2. Microtribological tests in contact to the diamond tip showed an almost linear increase of the amount of linear wear with increasing oxide thickness.

This result is in agreement with scratching experiments of a diamond tip on silicon carbide using the normal force of 60 µN [7]. Furthermore, oxide thickness on Si(111) and SiC samples after the tribological test was always significantly larger compared to the thickness of the equivalent native oxides (Fig. 7) of 1.5 and 1.0 nm, respectively. From these results and the finding, that the oxide thickness on the SiC samples resulting from the tribological interaction was independent of the oxidation treatment used, it may be concluded, that the oxide layers on the SiC samples were removed completely by the action of the diamond tip. By tribochemical activation of the SiC surface a new oxide layer was formed hereafter, showing a thickness about twice as high as that of the native oxide.
Assuming that wear was primarily caused by the abrasive action (micro-ploughing/microcutting) of the sliding diamond tip, then friction coefficient and amount of linear wear should increase with decreasing nanohardness of the surfaces. This agrees qualitatively with the experimental results.

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6 REFERENCES