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High Temperature Tribological Behaviour of Particulate Composites in the System SiC-TiC-TiB_2 during Dry Oscillating Sliding

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The tribological behaviour of monolithic SiC as well as SiC-TiC and SiC-TiC-TiB_2 particulate composite materials has been investigated in unlubricated oscillating sliding tests against Al_2O_3 at temperatures in the range from room temperature up to 600°C. At temperatures below 600°C the wear rate of the systems with the composite materials was up to 20 times lower than the wear of the Al_2O_3/SiC system and was dominated by the oxidation of the titanium phases. At 600°C the oxidation rate of the TiC and TiB_2 grains becomes predominant resulting in an enhanced wear rate of the composite materials. The coefficient of friction shows similar values for all materials of investigation, increasing from 0.25···0.3 at room temperature to 0.7···0.8 at 600°C. The wear of the Al_2O_3/SiC system is mainly abrasive at temperatures above room temperature and is characterised by an enhanced wear of the alumina ball at 600°C.

Key words : Ceramic Composites, High temperatures, Tribo-oxidation, Dry slidins, Friction, Wear

I. Introduction

Due to their unique combination of physical, chemical and mechanical properties, advanced technical ceramics are being used for tribological applications under severe conditions. Among the parameters influencing the tribological behaviour of sliding tribocouples the temperature is one of the most important. In this regard many ceramic tribocouples have been investigated mainly with the goal to understand high temperature wear mechanisms and to find material combinations for sliding applications at high temperatures.[1-7]

Tribo couples with ceramic particulate composite materials have shown a tribological performance superior to that of single phase materials in many cases at elevated temperatures. On one hand this is due to their superior mechanical properties, like enhanced bending strength and fracture toughness, but on the other hand also due to the capability to form wear or friction reducing tribochemical reaction products.[8,9] Silicon carbide materials show in general good mechanical strength and good oxidation resistance at elevated temperatures. However, as was shown in several investigations at room temperature,[10-12] TiC and TiB_2 dispersed within the SiC matrix can improve the wear resistance under unlubricated conditions against an Al_2O_3 or SiC counterbody considerably. Characteristically the friction coefficient was found to be relatively high around 0.5, although the wear of these tribocuples was reduced. The investigation of the wear mechanism in the tribocouples Al_2O_3 ball against SiC-TiC or SiC-TiC-TiB_2 showed that the formation of a mixture of soft oxides due to tribo-oxidation leads to a well adhering layer in the sliding interface thus reducing the wear.[13] Since tribo-oxidation is one of the main mechanisms influencing the wear properties of these tribo couples, the temperature is of special importance for wear and friction. Therefore, in this paper the tribological behaviour of SiC, SiC-TiC and SiC-TiC-TiB_2 sliding against an Al_2O_3 ball in air is investigated at temperatures up to 600°C. Al_2O_3 was chosen as an inert material with a high wear resistance, being easily available for comparative tests. The composition of the disk materials is the same as for those used in,[13] so that a direct comparison of the results will be possible.

II. Experimental Procedure

1. Materials and specimens

In Table 1 details of the investigated materials are summarised. Al_2O_3 (99.9%) balls are commercial products from Ceratec, Geldermalsen, NL.

The disk specimen with a diameter of 30 mm and a thickness of 4 mm were produced by a ceramic manufacturing process as is described in.[14] According to the composition, SiC, TiC, and TiB_2 powders were blended in the corresponding ratios and milled by attrition milling to the particle size necessary for sintering. SiC milling balls were used to guarantee a controlled purity and phase content of the sintered bodies. Sintering was carried out in a gas pressure sintering device at temperatures of about 2180°C with a holding time of 1 hour and an Ar pressure of 5 MPa. Only classical sintering aids for SiC sintering were used. After sintering the phase contents were controlled by X-ray powder diffraction. Neither phase

Table 1. Materials Data

Specimen geometry	Material	Phase Composition Mol %				Porosity %	Bending Strength, MPa	Fracture toughness, MPa $m^{1/2}$
		Al_2O_3	SiC	TiC	TiB_2			
Ball:	Al_2O_3	100	–	–	–	<1	400	4.0
Disk:	SiC	–	100	–	–	<2.5	380	3.6
	SiC-TiC	–	50	50	–	<1.5	445	5.7
	SiC-TiC-TiB_2	–	50	25	25	<1	460	5.7

reactions nor new phases were found. The sintered densities were measured by the Archimedes method. In all cases the density approached the theoretical values, as was verified by the optical investigation of the practically porefree microstructure. Only the SiC specimens had a closed porosity of about 2.5%.

2. *Tribotesting*

The friction and wear tests were performed with oscillating sliding motion in a oscillating sliding test rig (SRV tester, Optimol Instruments), described in more detail in,[15] working with a ball-on-disk configuration. With this tribometer tests can be performed with preselected operational parameters stroke, frequency and load in air up to temperatures of about 700°C. All tests were performed in laboratory air. The operational parameters used in the tests are compiled in Table 2.

During each test the coefficient of friction and the linear wear of the tribocouple are measured and recorded continuously.

The volumetric wear of both specimens was calculated separately after the test from the size of the wear scar at the pole of the ball and the planimetric wear at the disk, determined by profilometry with a diamond stylus. The following equations were used:[13]

Ball:

$$W_{v,ball} = \frac{\pi * d_1^2 * d_2^2}{64} * \left(\frac{1}{R} - \frac{1}{R'}\right) = \frac{\pi \quad d_2^2}{8} \quad W_{l,ball} \qquad (1)$$

Disk:

$$W_{v,disk} = \frac{\pi * d_1^2 * d_2^2}{64 * R'} + \Delta x * W_q = \frac{\pi * d_2^2}{8} * W_{l,disk} + \Delta x * W_q \qquad (2)$$

With:

d_1 =Diameter of the wear scar at the ball, perpendicular to the sliding direction
d_2 =Diameter of the wear scar at the ball, parallel to the sliding direction
R =Radius of the ball
R' =Radius of the curved wear scar, determined from the profile
$W_{l,ball}$=Linear wear at the ball
$W_{l,disk}$=Linear wear at the disk
Δx =Stroke (twice the amplitude)
W_q =Planimetric wear at the disk

Table 2. Test Conditions for Oscillating Sliding Eexperiments

Ball	Al_2O_3
Disk	SiC SiC-TiC SiC-TiC-TiB_2
Stroke	Δx=0.2 mm
Frequency	ν=10 Hz
Normal Force	F_n=10 N
Number of cycles	n=100,000
Temperature	25°C, 200°C, 400°C, 600°C

III. Results and Discussion

1. *Wear behaviour*

During each test a wear scar is produced at the pole of the ball as well as at the disk. Some typical wear scars at the disks are shown exemplarily in Fig. 1, produced in tests at 200°C and in Fig. 2 after tests at 600°C. Below the optical micrographs the corresponding profiles are shown, produced with a diamond stylus instrument across the middle of each wear scar. The planimetric wear W_q represents the area below the original surface and is used for the determination of the amount of worn off material (volumetric wear W_v).

The volumetric wear at ball and disk, calculated according to equations (1) and (2), is shown in Fig. 3 as a function of temperature.

For the Al_2O_3/SiC-TiC and Al_2O_3/SiC-TiC-TiB_2 tribo-couples and temperatures up to 400°C the wear at ball and at disk

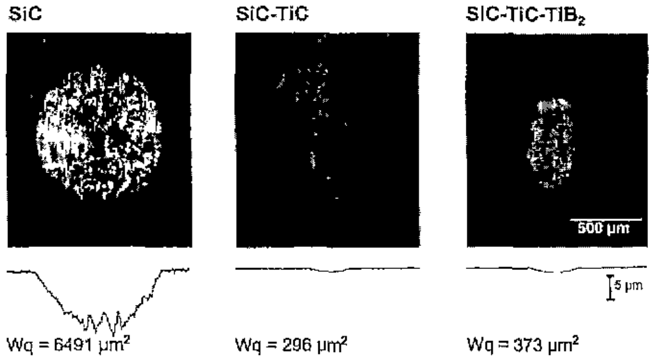

Fig. 1. Optical micrographs of wear scars on disk specimen after oscillating sliding tests against alumina ball at 200°C.

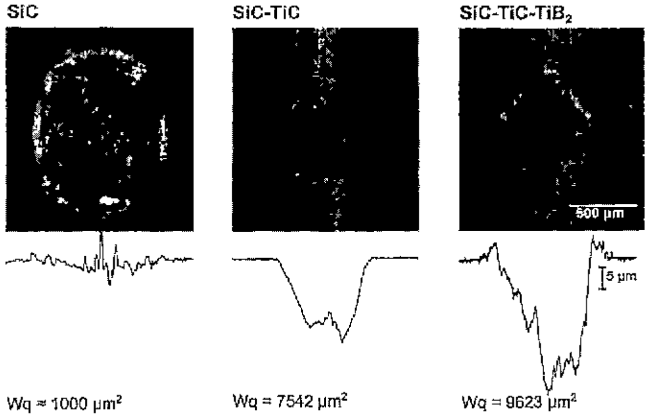

Fig. 2. Optical micrographs of wear scars on disk specimen after oscillating sliding tests against alumina ball at 600°C.

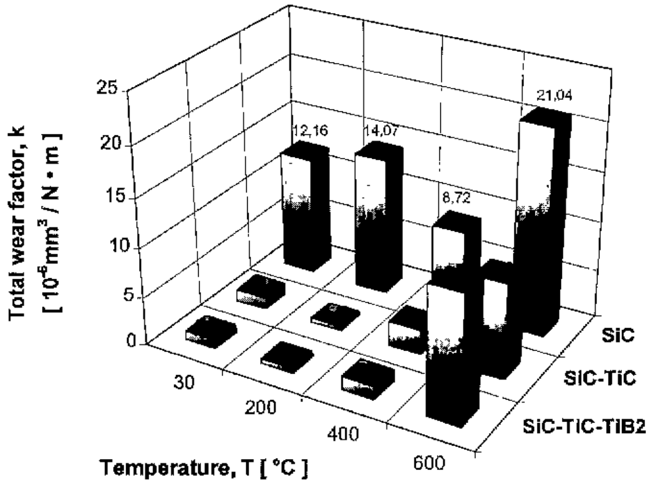

Fig. 4. Total wear factor for tests with alumina ball against SiC-composites versus temperature.

is in both cases similar and relatively small. This is in agreement with the results in[13] and can be interpreted by the formation of soft wear reducing tribo-oxidative layers. Characteristically for these two pairings, the volumetric wear of the disk is increasing drastically at 600°C, whereas the wear of the ball remains very low or even decreases close to the limit of resolution. As a consequence the Hertzian contact area remains small, too, thus keeping contact pressures high during the entire test. As can be seen in Fig. 2 the diameter of the wear scars is relatively small but the disk material is worn considerably in the depth.

For the Al_2O_3/SiC tribocouple the disk wear exceeds that of the ball up to 400°C. However, above 400°C the wear at the alumina ball increases considerably, while the wear at the disk is reduced further. At 600°C the wear of this system is thus mainly determined by severe wear of the ball. Contrary to the two tribo couples with the composite materials, the initially high contact pressure in this case is decreasing rapidly with time due to the increase of the contact area.

Fig. 4 shows the total wear factor k, describing the wear of the system, for all three tribocouples investigated at temperatures of 30 (room temperature), 200, 400 and 600°C, respectively.

The total wear factor of the tribo couples with the composite materials is at all temperatures smaller than for tests against the pure SiC disk. For the room temperature investigation this result is in good agreement with the earlier investigation, carried out on a different tribometer.[13] At 200°C the total wear of the tribocouples with both SiC-TiC and SiC-TiC-TiB$_2$ disk is even smaller than for room temperature, but increases by a factor of 5 to 10 when temperature increases from 400°C to 600°C. the wear of the tribo couple with the SiC disk is slightly increasing up to 200°C and then decreasing marginally at 400°C due to decreasing wear of the disk At 600°C the wear of this system increases again by more than a factor of 2 because of the drastically increasing wear of the alumina ball, whereas the disk wear is decreasing.

2. *Friction behaviour*

The evolution of friction coefficient f, defined as the

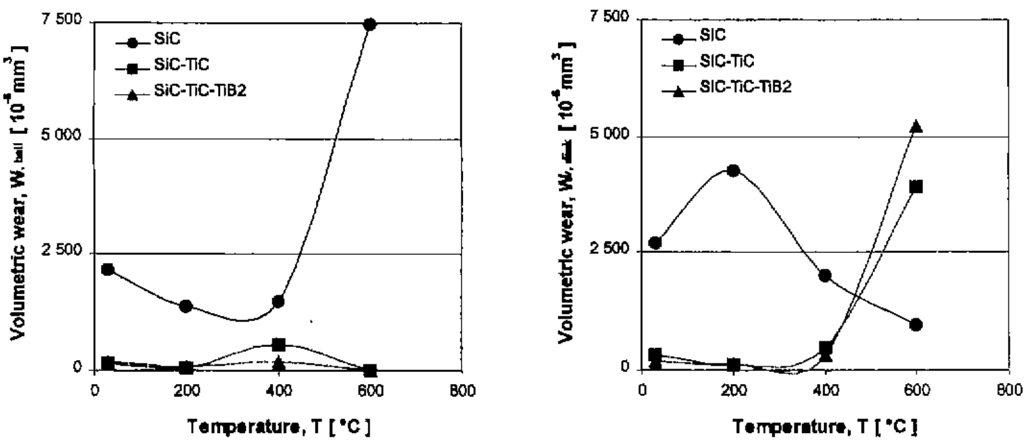

Fig. 3. Volumetric wear at the ball (left) and disk (right) versus temperature.

ratio of friction force and normal force, is shown in Fig. 5 for tests at room temperature and in Fig. 6 for tests at 600°C.

For the Al_2O_3-SiC pairing at room temperature the tribological behaviour can be characterised as a tribo-oxidative mechanism, causing formation of unstable tribo-reaction layers in the presence of water vapour in the surrounding atmosphe.[13,18,22] The formation of these unstable tribo-reaction layers in the test with SiC can be deduced from Fig. 5 (top). These layers are relatively smooth but do not adhere well. The oscillations of the coefficient of friction are due to a nearly periodically process of forming and wearing off of reaction layers.[13] At 600°C, however, no formation of tribo reaction layers is indicated.

For all three couples of investigation the mean value of friction coefficient is on a level of 0.3 at room temperature and roughly twice this value at 600°C. The compilation of all friction values versus temperature is shown in Fig. 7. The coefficient of friction increases from values in the range from 0.25 to 0.32 at room temperature to values of $\cong$0.7 at 400°C to 600°C. The relatively low values at room temperature are mainly influenced by the water vapour as observed in earlier investigations.[10,11] At higher temperatures the coefficients of friction are typical for pure solid state sliding and also consistent with experimental results in similar ceramic composite systems.[3,8,9,16,17] Anyway, these high friction values point at the fact, that no low friction mechanisms are activated.

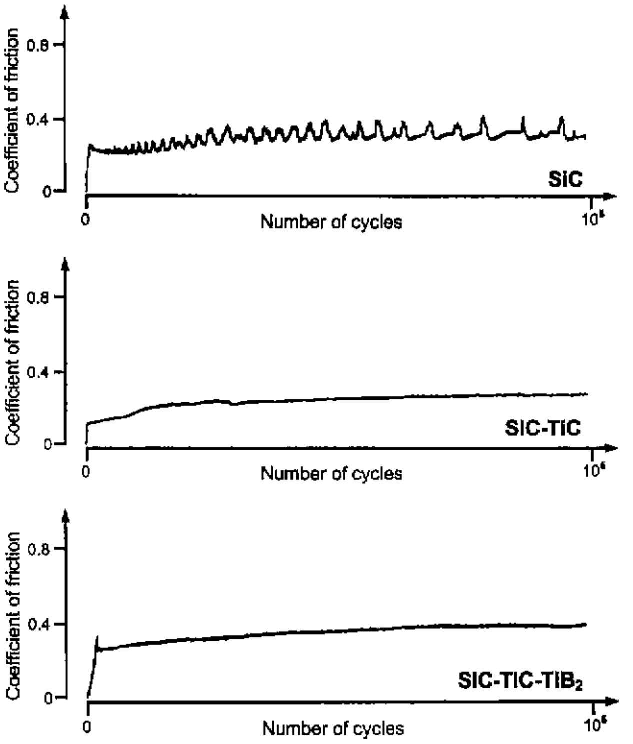

Fig. 5. Coefficient of friction versus number of cycles for oscillating sliding of SiC (top), SiC-TiC and SiC-TiC-TiB_2 (bottom) against Al_2O_3 at room temperature (30% R.H.).

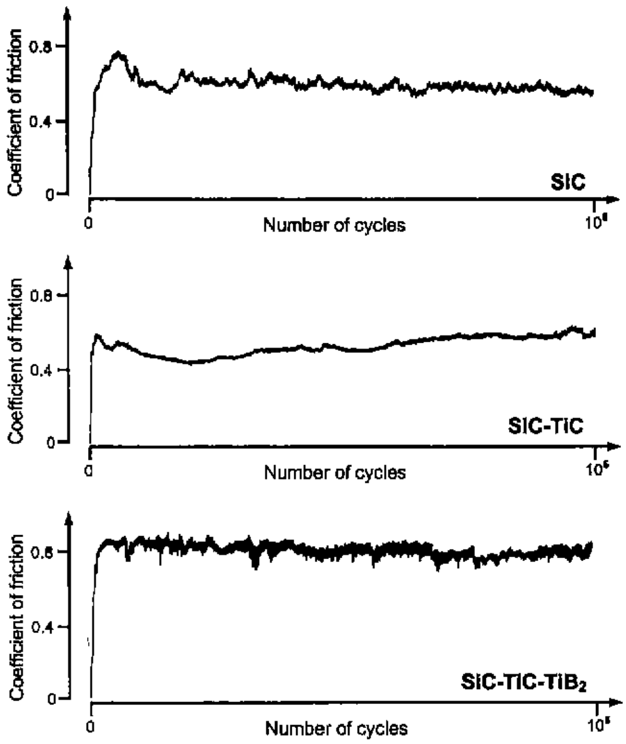

Fig. 6. Coefficient of friction versus number of cycles for oscillating sliding of SiC (top), SiC-TiC and SiC-TiC-TiB_2 (bottom) against Al_2O_3 at 600°C.

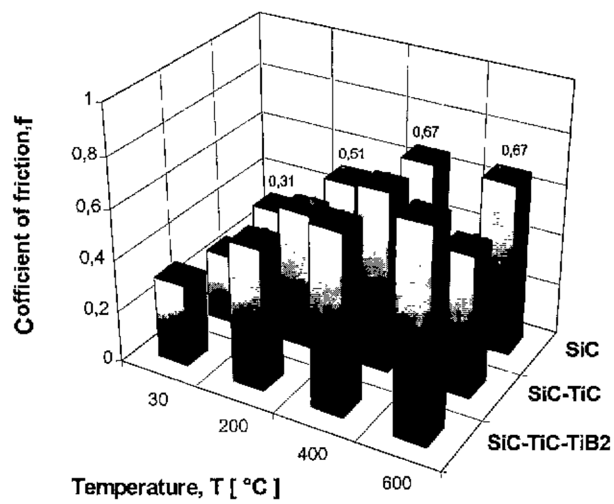

Fig. 7. Coefficient of friction for tests with alumina ball against SiC-composites versus temperature.

3. *Microanalytical investigations*

Fig. 8 shows a SEM micrograph of the characteristic inner part of the wear scar on the SiC disk after a test against the alumina ball at 400°C. This part of the wear scar is relatively rough, pointing at the same abrasive wear mechanism as observed for room temperature,[13] resulting in the formation of brittle abrasive oxide

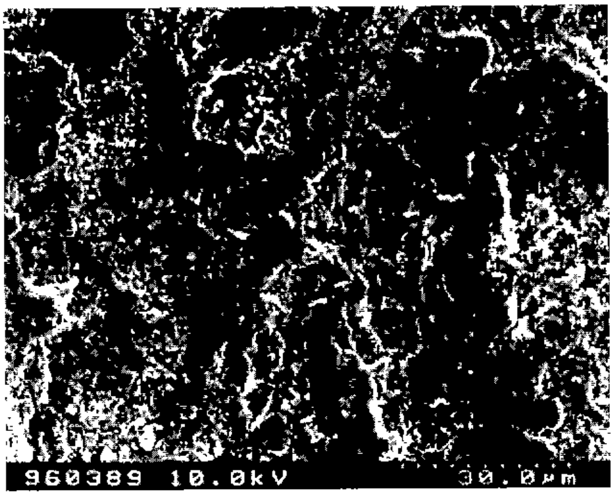

Fig. 8. SEM micrograph of a characteristic rough inner part of the SiC wear scar after test against Al_2O_3 at 400°C covered with Al_2O_3 wear debris.

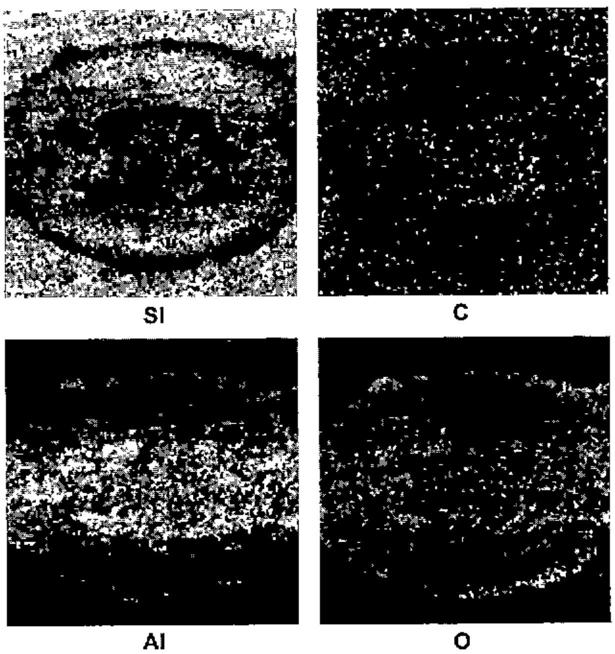

Fig. 9. Element mapping of Si, C, Al and O of the SiC wear scar after test against Al_2O_3 at 400°C.

particles within the interface, either due to the oxidation of SiC from the disk or due to the wear of the alumina ball. Fig. 9 shows an element mapping of silicon, carbon, aluminium and oxygen in this wear scar, revealing that the rough inner area consists mostly of Al_2O_3 and SiC wear debris and to a minor content of SiO_2, whereas the smoother outer part consists mainly of the polished primary SiC. At the outer edge of the wear scar also Al_2O_3 wear debris is concentrated.

Figs. 10 and 11 show characteristic areas of the oxide film which has been formed in the Al_2O_3/SiC-TiC-TiB_2 interface during sliding at 400°C (Fig. 10) and 600°C (Fig.

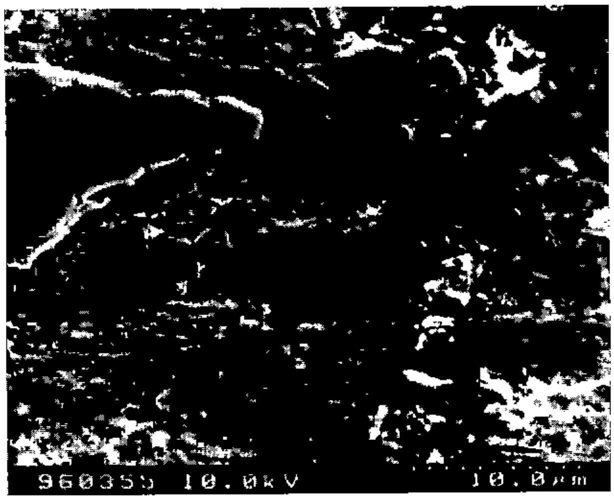

Fig. 10. Characteristic area of oxide film formed in the Al_2O_3/SiC-TiC-TiB_2 interface during sliding at 400°C.

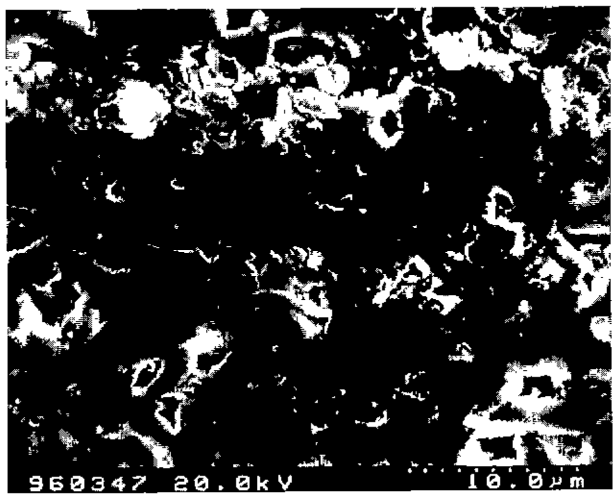

Fig. 11. Characteristic area of oxide film formed in the Al_2O_3/SiC-TiC-TiB_2 interface during sliding at 600°C.

11). The thickness of the oxide layer is relatively thin, so that the microstructure of the bulk material is appearing. Fig. 12 shows the element mapping for silicon, titanium, aluminium and oxygen of the wear scar on the SiC-TiC-TiB_2 disk after a test at room temperature and Fig. 13 shows that one after a test at 400°C. The in difference is observed in the oxygen distribution. In the room temperature wear scar oxygen is mainly connected to Al_2O_3 and TiO_2 wear debris located in some oxide reservoirs. The primary SiC and TiC grains of the microstructure, if at all, are only silightly covered by an oxide layer thus forming the wear reducing oxide film. This is consistent with the results reported in[13] that the lubricious soft oxide mixture is located in the reservoirs of the surface. At 400°C, as shown in Fig. 11, oxidation is much more severe, but mainly oxidation of the titanium phases occurs.

The silicon and titanium distribution represent the primary SiC, TiC and TiB_2 grains in the microstructure.

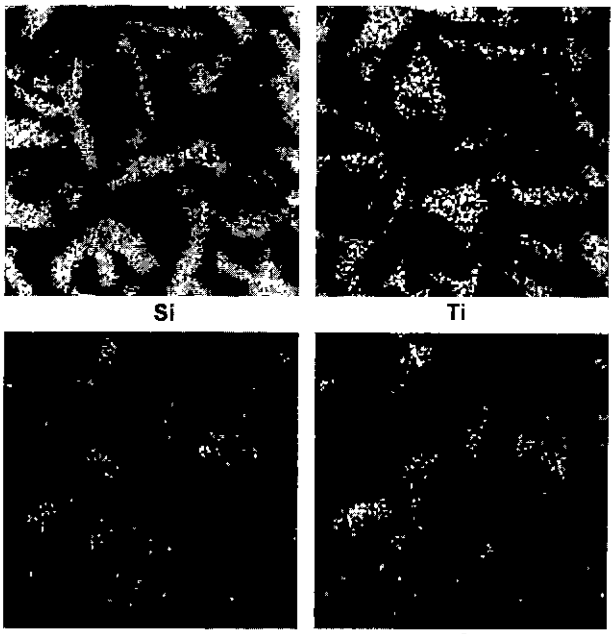

Fig. 12. Element mapping of Si, Ti, Al and O on the SiC-TiC-TiB_2 wear scar after test against Al_2O_3 at room temperature.

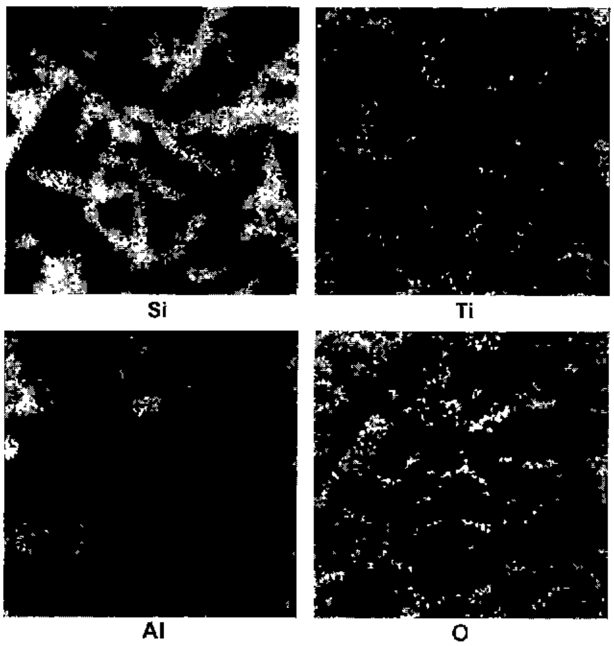

Fig. 13. Element mapping of Si, Ti, Al and O on the SiC-TiC-TiB_2 wear scar after test against Al_2O_3 at 400°C.

But besides the main concentration in the grains a small amount of these elements is distributed all over the wear scar as Si and Ti oxides. Aluminium in the form of oxide is spread over the surface but also found to a small extend, concentrated in some reservoirs.

Although oxygen in form of oxides is covering the surface, it is found in a higher concentration on the TiC and TiB_2 grains. In accordance with the SEM micrographs in Figs. 10 and 11 the surface film is relatively thin and a relatively thick oxidation zone is found on the TiC and TiB_2 grains. The distribution of boron could not be detected with sufficient accuracy.

4. Wear mechanisms

The experimental results obtained so far give evidence for different wear mechanisms being effective in the different tribo couples at different temperatures.

For the Al_2O_3-SiC pairing at room temperature the wear can be characterised as tribo-oxidative mechanism, causing formation of unstable tribo-reaction layers in the presence of water vapour in the surrounding atmosphere.[15] However, at 600°C as seen from the wear scar profile in Fig. 2, the wear of the system is mainly determined by the wear of the ball and most probably the mechanism is of abrasive character, due to the relatively hard and brittle Al_2O_3, SiC and SiO_2 wear debris. From the evolution of the coefficient of friction at 600°C, Fig. 6 (top), no formation of tribo reaction layers is indicated. As indicated by the rough areas in the wear scar as observed in SEM (Fig. 8) and the alumina debris seen in the electron mapping of Fig. 9 the wear mechanism at this temperature is abrasive in its character.

For the tribocouples with the composite disks in both cases wear is determined mainly by the oxidation of the titanium phases. In accordance with the modified wear model of Quinn[20,21]-as outlined in[13]-it may be deduced that the temperature increase mainly results in an increased oxidation rate preferentially of the Ti phases. This leads to an in-depth oxidation of the disk. Since the formed oxide is soft, the wear of the alumina ball is very small (Fig. 3, left). As a consequence the contact pressure remains high during the whole experiment. As long as the oxidation rate is low enough, from 30 to 400°C, the wear rate remains relatively low, because the bulk material of the disk is not deteriorated and therefore can bear the high contact pressure. This is in accordance with friction coefficients representing stable tribo reaction layers as shown in Fig. 5. However, when the oxidation of the titanium phases becomes predominant, the microstructure of the disk material cannot bear the high contact pressures and wear at the disk is increased drastically. The wear scars of Fig. 2 show therefore the in depth wear of the disks.

The wear of the composite materials is thus mainly dependent on the oxidation rate during sliding. Since the sliding velocity is relatively small in the order of 0.01 m/s, frictional heating is negligible. Therefore the temperature of the environment is mainly determining the oxidation rate. In that case the wear rate should be reversible, that means that the wear rate should be reduced again when the temperature is decreased. This assumption was proven experimentally by repeating the room temperature tests after finishing the sliding experiments at high temperatures. The coefficient of wear as well as the coefficient of friction were very similar to those ones measured at room temperature before the exposure of the tribo couple to high temperatures.

IV. Conclusions

The wear behaviour of tribo couples with composite materials SiC-TiC and SiC-TiC-TiB_2 is significantly different from tribo couples with SiC and is superior at all investigated temperatures to Al_2O_3/SiC. For Al_2O_3/SiC the wear is abrasive in its character at all temperatures, causing wear of ball and disk. At 600°C the wear of the alumina ball is drastically increased thus determining the wear of this system.

The wear of the tribo couples with composite materials is characterised by the oxidation of TiC and TiB_2 but depending on the oxidation rate. At temperatures up to 400°C the oxidation rate is low and the formation of relatively soft titanium oxides leads to the formation of an oxide film and subsequently to low wear at ball and disk. However, at temperatures of 600°C in the ambient the increased oxidation rate of TiC and TiB_2 grains leads to drastically increased wear of the disk material.

Acknowledgments

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