

Wear Resistance of α SiC–TiB₂ Composites Prepared by Reactive Sintering

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Abstract

The relative wear resistance of α SiC–TiB₂ composites prepared by reactive sintering was investigated on a pin on flat tribometer, in air and in presence of water. Experimental results show that the composite materials are less worn than monolithic SiC. The wear mechanisms in air and water are identified.

In air, a protective oxidised debris layer is formed on the composites, whereas roller formation was observed with SiC. In water, the surface of the composites is polished, whereas SiC is worn by fragile ruptures (cleavages). © 1999 Elsevier Science Limited. All rights reserved

Keywords: SiC, borides, wear resistance, composites, reactive sintering.

1 Introduction

Silicon carbide ceramics are widely used for tribological applications (water pump bearings for cars, diverse wear devices, fiber guides...).¹ Silicon carbide has a low friction coefficient ($f < 0.1$ in liquids), very high hardness (22 GPa), high thermal conductivity (180 W/mK at 20°C) and excellent corrosion resistance.

Numerous studies have been carried out on the tribological behaviour of monolithic ceramic materials, but few have been devoted to composites materials. Most of them concerned with whiskers containing composites² or metal matrix composites reinforced with particles.^{3,4}

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Concerning monolithic SiC, most authors describe its smooth and polished surface.⁵ The worn surface is finely grooved. Some of the researches evoke micro-chipping, or grooves which proceed perpendicularly, to the direction of the displacement sliding.

Hsu *et al.*⁶ carried out an extensive study on SiC by establishing wear maps, identifying wear transitions depending on the environment, the velocity and normal force applied. At low speeds and under low loads, in air or water, material is eliminated by microabrasion. For intermediate speeds and loads, in air and water, wear is due to intergranular fracture. Finally for high speeds and loads, wear in air is due to intragranular fracture, whereas in water the intergranular rupture mechanism is maintained.

Concerning the SiC matrix composites, wear depends on the dispersion nature. Indeed with TiC additions, worn surfaces in air are characterized by wear particles adhesion, plastic deformation and tribo-oxidation.⁷ For composites SiC/ZrB₂ + B₄C, after frictioning the surfaces in air, no cracking occurs on the sliding surfaces, but only polishing and grooving are observed. In water, fine grooves are observed.⁸ And finally with TiB₂ dispersions, in air the following mechanisms are observed:⁹

1. cracking of the weak TiB₂ particle/SiC matrix interface at the beginning of wear
2. cracking of the matrix, perpendicularly to the direction of sliding
3. possible chipping of the surface and grain pullout.

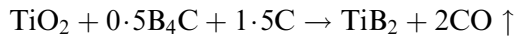
For liquid-phase sintered SiC–TiB₂ composites,¹⁰ wear is initiated by a grooving process, followed by a grain pullout process.

This paper reports the wear behavior of SiC–TiB₂ composites prepared by reactive sintering, in

air and in the presence of water. SiC was used as a reference material.

2 Experimental Procedure

Concerning the elaboration, the starting materials were α SiC, TiO₂, B₄C powders and a resin as carbon source.^{11,12} After milling of powders in water, drying and sieving, reactive sintering without pressure was carried out. The reaction was the following:



The properties and characteristics of the materials are described in Table 1.^{11,12}

The microstructure of the materials is described elsewhere¹²: the mean grain size of SiC is 3–6 μm , whereas TiB₂ particles are mainly submicronic.

Concerning the wear behavior of the materials, wear tests were carried out using a reciprocating pin-on-flat tribometer [Fig. 1(a)]. The linear speed was 10 mm/s, and the normal load F_N was about 80 N. The stroke length was 5 mm. By measuring the tangential force F_T during the test, we evaluated the friction coefficient $\mu = F_T/F_N$.

The SiC balls (\varnothing 6 mm) produced by Saphir Werk Industrie Produkte AG, Brügg CH) and the SiC flats (SiC-100, from C & G, Bazet, F; pure α phase, mean grain size 5 μm , $d > 96.5\%$) were current industrial materials. The balls were industrially polished, whereas the flats were diamond polished up to $R_a \approx 0.01 \mu\text{m}$. The SiC–TiB₂ composites flats were also polished ($R_a \approx 0.01 \mu\text{m}$). The composites pins were hemispheric prepared by hot-pressing, and used as sintered.

Wear volume and surface are defined in Fig. 1(b)–Fig. 1(c). Because it was not easy to precisely measure the wear trace D on the flats, due to the stacking of debris, we chose to determine the surface S , instead of the real wear volume: it is legitimate for comparisons. The different parameters are determined as follows:

- a, R by optical microscopy
- P, L by profilometry
- h calculated

For symmetrical couples i.e. same materials, then for asymmetrical couples i.e. composites/monolithic SiC, wear tests are performed in air (relative humidity 40%) and in water; the temperature is not controlled.

The reproducibility of measures is near 10%.

3 Results

3.1 Symmetrical couples

3.1.1 Results of wear in air

Wear results of symmetrical couples are given in Fig. 2.

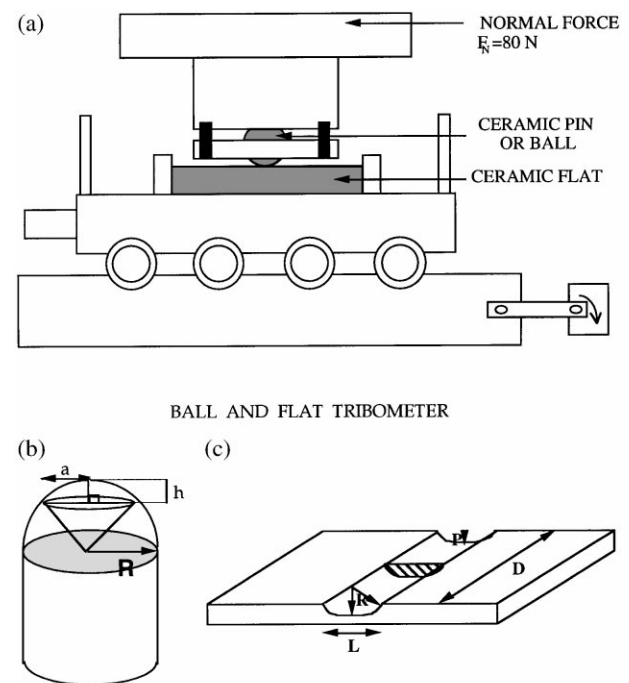


Fig. 1. (a) Pin on flat tribometer. (b) Wear volume of pins or balls $V(h, a) = \frac{\pi}{6}h(h^2 + 3a^2)$ with $h = R - \sqrt{R^2 - a^2}$. (c) Wear surface of tracks on flats $S = R^2 \times \text{Arcos}(\frac{R-P}{R}) - L \times \frac{R-P}{2}$ with $R = \frac{P^2 + L^2}{2P}$.

Table 1. Properties of materials

Materials	Sintering temperature	% Density	% of TiB ₂ (1) particles < 1 μm	Hardness (2) (GPa)	Toughness (3) $\text{MPa}\sqrt{\text{m}}$
SiC	—	97	—	22 \pm 1	3.2 \pm 0.3
SiC—	2190°C	98	75	30 \pm 1	3.6 \pm 0.4
5 vol% TiB ₂	1 h				
SiC—	2190°C	97	60	27 \pm 1	3.65 \pm 0.4
10 vol% TiB ₂	1 h				
SiC—	2190°C	95	55	23 \pm 2	3.95 \pm 0.4
15 vol% TiB ₂	1 h				

(1) Image analysis method;

(2) Vickers microhardness (5 N, 30 s);

(3) Vickers indentation fracture method (10 N, 30 s).

For the pins, we observed that SiC is less worn than all the composites [Fig. 2(b)].

On the contrary, for the flats, the composites are less worn than SiC. Therefore, wear decreases when the TiB₂ content increases [Fig. 2(a)].

We can explain that by the microstructures of the worn surfaces. First, for the composite flats, at 1 min test, all the flats are covered by a thick layer of debris, constituted by agglomerated particles (third body). These layers contain titanium, silicon and oxygen (EDS analysis) for the composites, oxygen and silicon for SiC materials. Then, the layer is eliminated from the interface, but some debris fill the roughness and porosity created by wear [Fig. 3(a)], and so protect the surfaces. On the other hand, SiC flat wears in another way: we observe intragranular fracture (cleavages), with a large production of debris, which can explain high wear. Then the debris are crushed, agglomerated and form rollers [Fig. 3(b)]. One assumes they are composed of amorphous SiO₂ resulting of the SiC oxidation.¹³ But in spite of their good load carrying capacity, as these rollers are simultaneously formed and eliminated in the contact, the wear is high.

For the composite pins, we can observe wear debris accumulation on the wear track, but then these debris are detached, and the wear is abrasive [Fig. 4(a)]. And finally, SiC ball wears less than composites pins because there are rollers on the

counterbody SiC flat; they protect its surface [Fig. 4(b)].

3.1.2 Results of wear in water

Wear results are given in Fig. 5

We can observe that water reduces the wear of all the materials. Moreover the friction coefficient μ is decreased by water.

For both pins and flats, composites are less worn than SiC. Therefore, the wear of pins decreases when the TiB₂ content increases.

Indeed, composites flats are polished smooth [Fig. 6(a)], whereas SiC flats contain an important intragranular fracture (cleavages) [Fig. 6(b)]. This can explain the low wear of composites and the high wear of SiC.

Therefore, for the pins, in the 5 vol% TiB₂ pins, some grains are pulled out, whereas for the 10 and 15 vol% TiB₂ pins [Fig. 7(a)], a layer of oxidized debris protects the surface, which decreases the wear. On the contrary, a great pulled-out of grains occurs on SiC balls [Fig. 7(b)].

3.1.3 Conclusion

Generally, we can notice that SiC wears a lot, it wears by cleavages (brittle rupture). On the contrary, the formation of rollers decreases the wear rate.

For the composites, the stable agglomeration of the oxidized third body in the interface seems to be

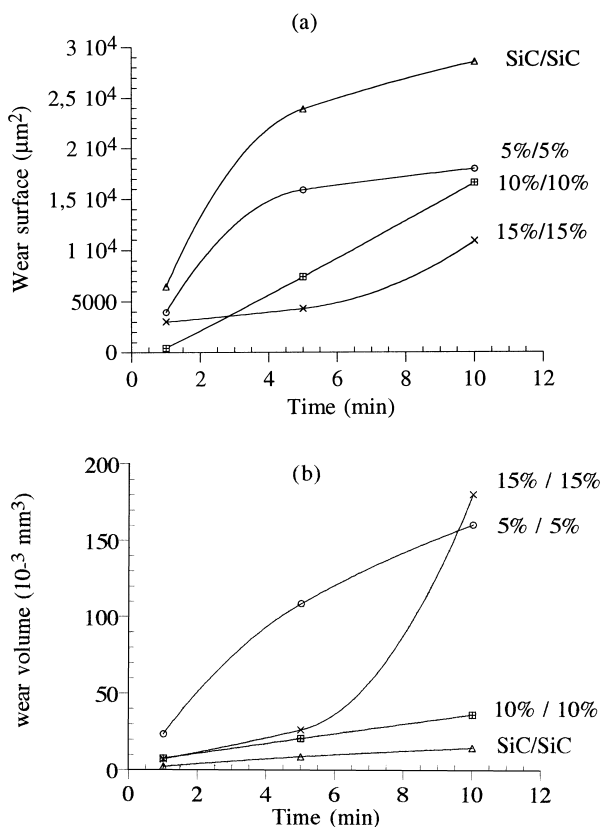


Fig. 2. Wear of flats (a) and pins (b) in air, for symmetrical couples (1 min \leq \leq 0.6 m).

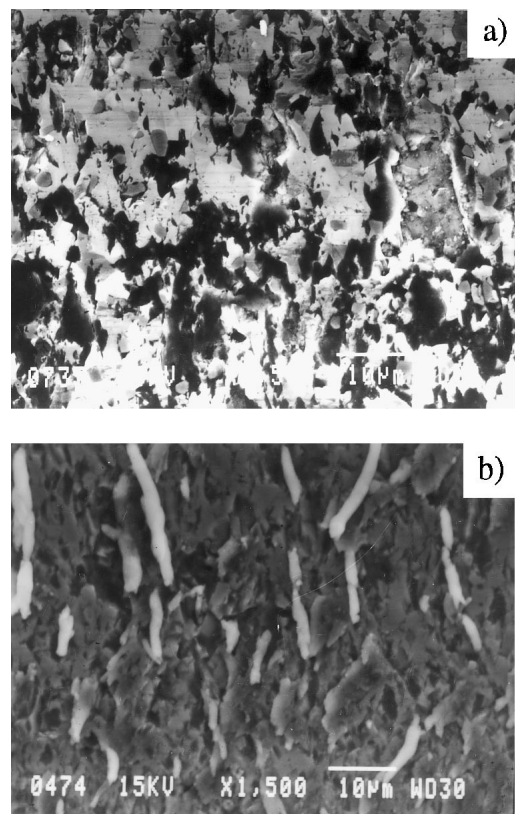


Fig. 3. Worn surfaces of flats (symmetrical couples in air) (10 min sliding). (a) Composite flats: rugosity filled by oxidized debris. (b) SiC flats:rollers.

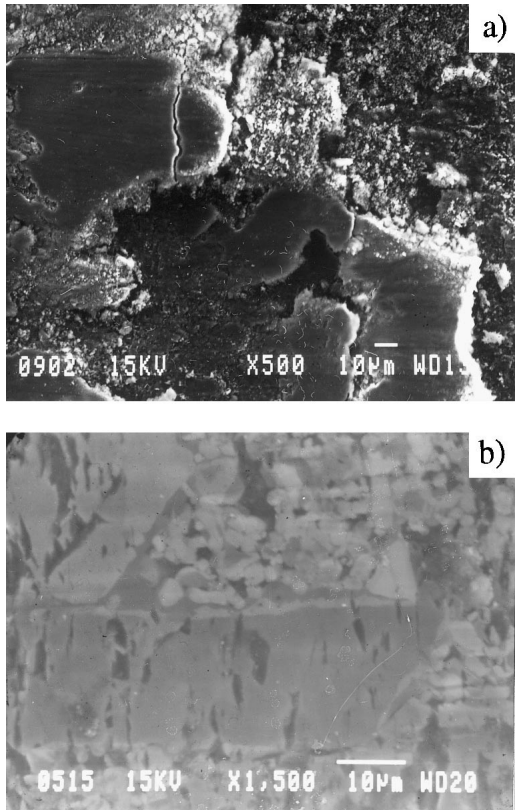


Fig. 4. Worn surfaces of pins (a) and balls (b) (symmetrical couples in air). (a) Composite pins: unstable thick layer of debris. (b) SiC ball: polished surface.

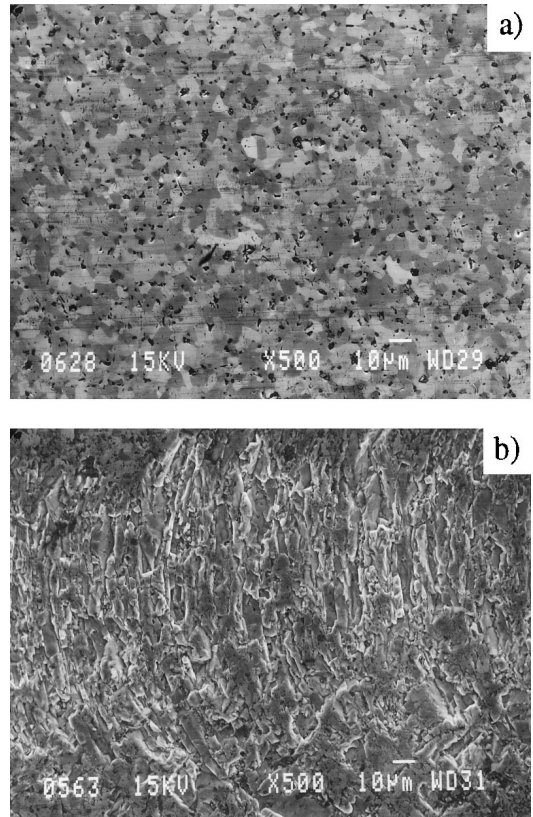


Fig. 6. Worn surfaces of flats (symmetrical couples in water). (a) Polished surface of composite flats. (b) Cleavages in SiC flats.

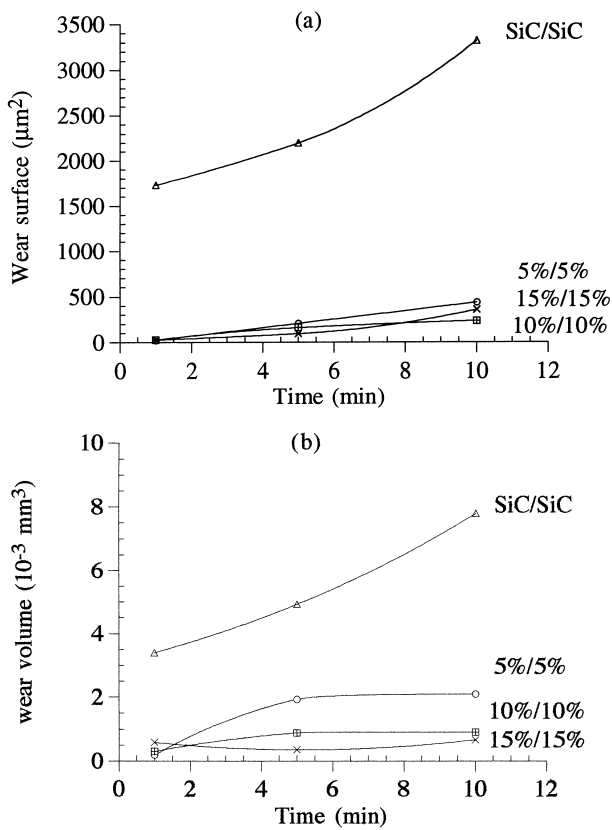


Fig. 5. Wear of flats (a) and pins (b) in water, for symmetrical couples (1 min < = > ; 0-6 m).

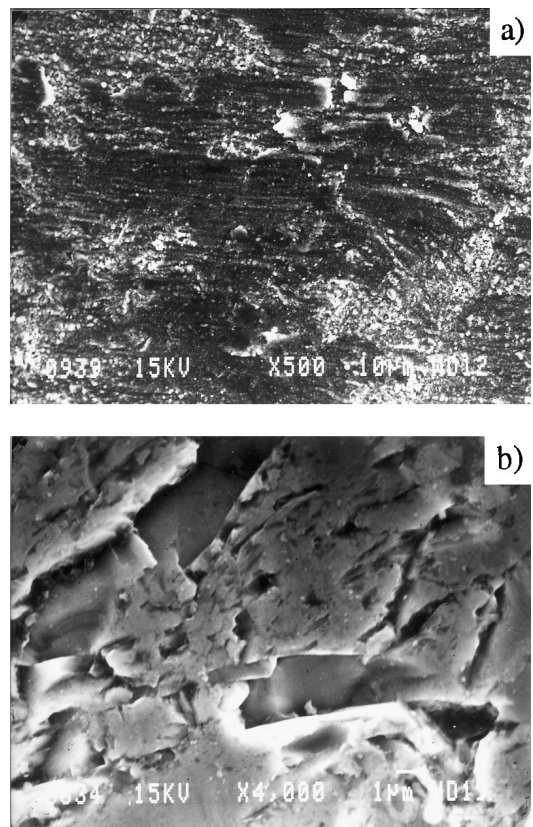


Fig. 7. Worn surfaces of composite pins and SiC balls (symmetrical couples in water). (a) Protective layer of debris on composite pins (10 an 15 vol% TiB₂) (b) Pull-out of large grains on SiC balls.

protective for the surfaces. But, when the third body is not stable, wear is abrasive and severe.

3.2 Asymmetrical couples: SiC balls on composite flats

3.2.1 Results of wear in air

Wear results are given in Fig. 8.

The SiC ball seems to wear less against 5 vol% TiB₂ flat than against the others [Fig. 8(b)].

For the flats, SiC flat wears more than composite flats [Fig. 8(a)]. (SiC ball-SiC flat is always the reference couple.)

The examination of friction coefficient μ (Fig. 9) gives information on the behavior of the debris in the interface: when the wear debris are removed from the interface, the friction coefficient decreases.⁵

In the case of composite flats, a thick and stable third body, containing titanium and oxygen (EDS analysis), is formed. During the first minute of the test this third body agglomerates and then protects the surfaces, which is the case for the 5 vol% TiB₂ [Fig. 10(a)]. For 10 and 15 vol% TiB₂, the third body is less stable and wear is more severe.

For SiC flat, as we have just seen, rollers formation by cleavages leads to an important wear [Fig. 3(b)].

In the case of the SiC ball, it wears less against 5 vol% TiB₂ flat, because the debris on the antagonist flat are stable and protect its surface [Fig. 10(b)].

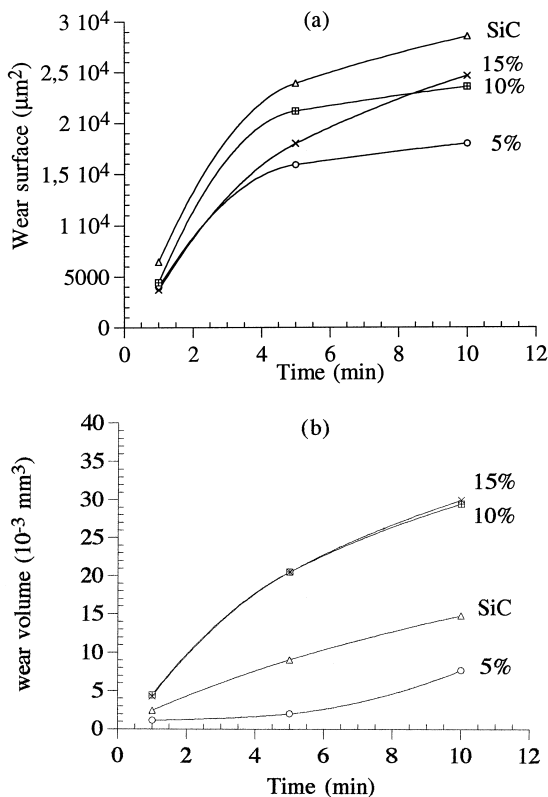


Fig. 8. Wear of composite flats (a) and SiC balls (b) for asymmetrical couples, SiC ball/composite flats, in air.

In the other case (10 and 15 vol% TiB₂), debris are eliminated, that increases the wear of the ball.

Finally, in the case of friction against SiC (symmetrical couple), as we have just seen, rollers on the antagonist SiC flat protect the SiC ball [Fig. 4(b)].

3.2.2 Results of wear in water

Wear results are given in Fig. 11.

For both balls and flats, composites wear less than SiC. Therefore, wear and also the friction coefficient (Fig. 12) decreases when the TiB₂ content increases.

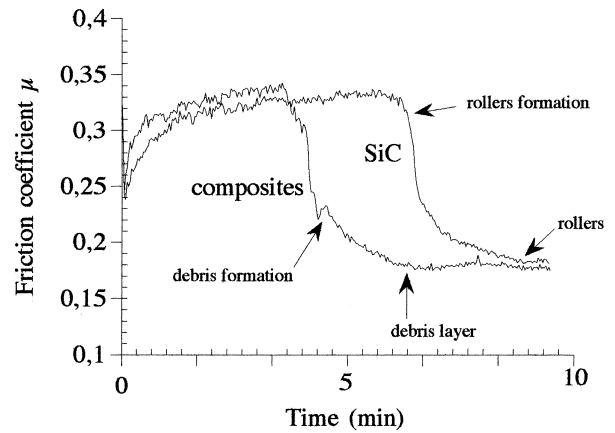


Fig. 9. Friction coefficient of asymmetrical couples SiC ball/composite flats, in air.

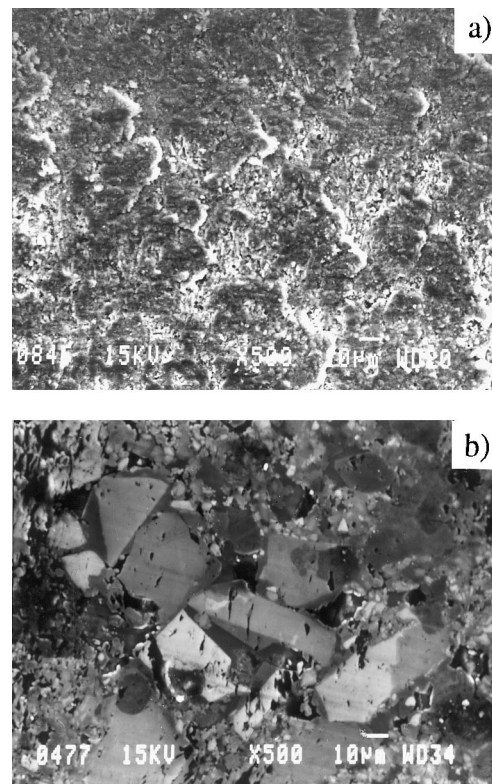


Fig. 10. (a) Stable third body on 5 vol% TiB₂ flat (asymmetrical couple; SiC ball/composite flats, in air). (b) surface of the SiC ball after friction against 5 vol% TiB₂ in air.

On the composite flats, we can observe circular cracks [Fig. 13(a)], whose spacing increases with the TiB_2 content. Swain¹⁴ has related the space between two adjacent cracks to the coefficient of friction: it is small when the coefficient of friction is high.

It is what we experimentally observe: the space between cracks increases with the TiB_2 content, whereas friction coefficient decreases.

For SiC flat, as we have already seen, cleavages lead to high wear. Finally, for the SiC balls, in the case of friction against composite, the surface is rather polished [Fig. 13(b)], whereas in the case of a friction against SiC, important pulled-out of grains occurs.

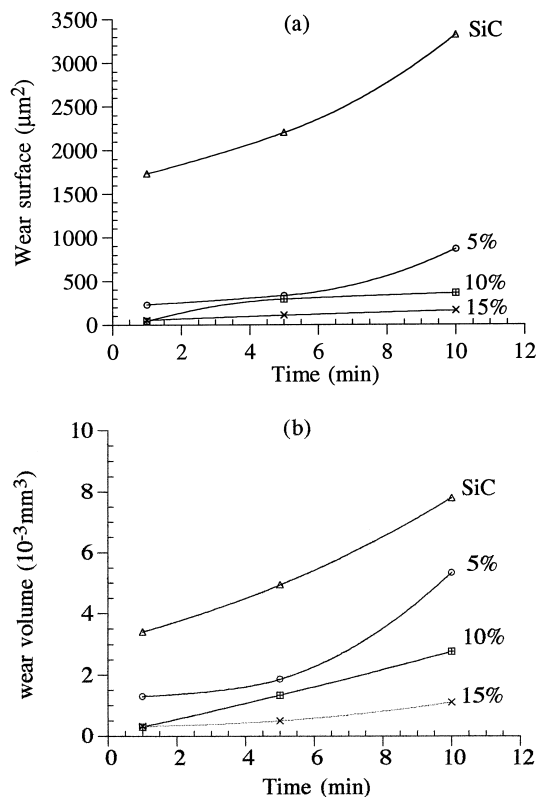


Fig. 11. Wear of composite flats (a) and SiC balls (b) for asymmetrical couples SiC balls/composite flats in water.

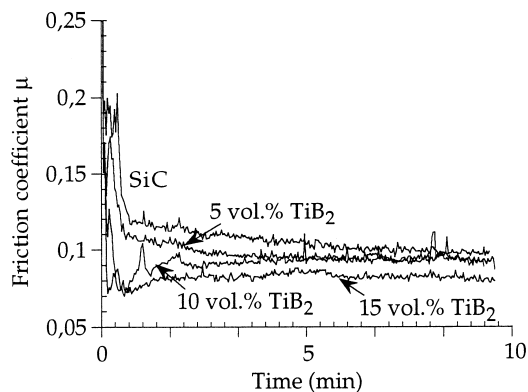


Fig. 12. Friction coefficient of asymmetrical couples SiC balls/composite flats in water.

3.2.3 Conclusion

As for symmetrical couples, the formation of stable and oxidized debris on composite flats in air protect the surface. In water, the third body is eliminated, but wear is not severe.

SiC ball can be protected by the third body on the antagonist flat (air) or be polished (water).

3.3 Asymmetrical couples: composites pins/SiC flat

3.3.1 Results of wear in air

Wear results are given in Fig. 14.

For the pins, the wear of the pin increases when the TiB_2 content increases.

Pure SiC ball is less worn than all the composites [Fig. 14(b)].

For the flats, we cannot classify the ceramics with the TiB_2 content [Fig. 14(a)].

For the flats, the observation of the track gives two kinds of behavior:

- in the case of friction against composite pins, the debris (oxidized, containing titanium) form and accumulate in the center of the track [Fig. 15(a)] whereas the center of the track is polished.
- in the case of friction against SiC ball, as we have already seen, there is formation of rollers.

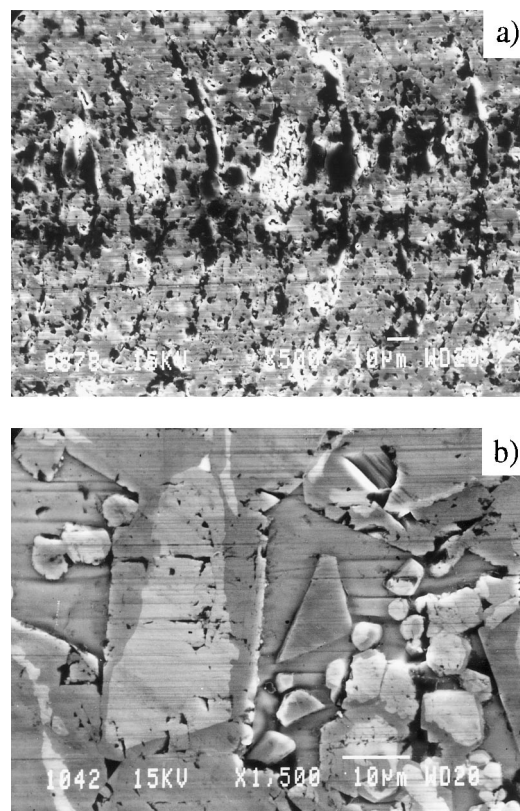


Fig. 13. circular cracks on 15 vol% TiB_2 flat (asymmetrical couples: SiC ball/composite flats in water). (b) Worn surface of SiC ball (friction against 15 vol% TiB_2 flat).

For the composites pins, at the beginning of the test, debris agglomerate to form a thick layer. Then they are eliminated from the contact, and the surface of the pin is no more protected. We can observe

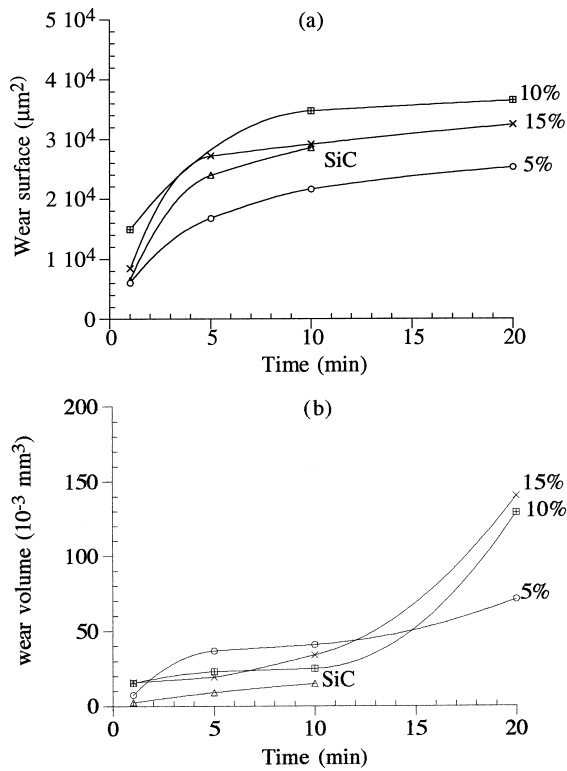


Fig. 14. Wear of SiC flats (a) and composite pins (b) for asymmetrical couples composite pins/SiC flats in air.

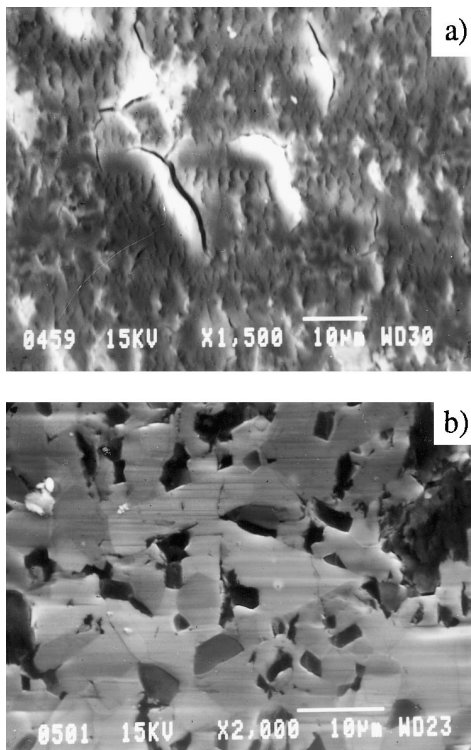


Fig. 15. (a) Agglomeration of oxidized debris on SiC flat (asymmetrical couples: composite pins/SiC flats in air). (b) Chipping of grains, filling of rugosity by debris on composite pins.

chipping of grains, and the filling of the porosity created by wear by oxidized debris [Fig. 15(b)].

The wear is more severe because of chipping of grains. As we have already seen, the SiC ball is less worn than the composite pins, because of rollers formation on the antagonist flat.

3.3.2 Results of wear in water

Wear results are given in Fig. 16.

We can see that wear decreases when the TiB₂ content increases for both pins and flats.

SEM observations show that the SiC flat is polished, with some circular cracks in the center of the track [Fig. 17(a)] when the antagonist is a composite, whereas the flat is fractured when the antagonist is SiC, as we have already seen [Fig. 6(b)].

Wear mechanisms for composite pins are the following: at the beginning of the wear, pin's surface is covered by oxidized debris; then this third body is eliminated and the surface is polished. Some pull-out of grains appears [Fig. 17(b)].

On the contrary, as we have already seen, the wear of the SiC ball occurs by an important pull-out of large grains, which leads to severe wear [Fig. 7(b)].

3.3.3 Conclusion

In air, in the case of friction of composite pins against SiC flat, oxidized debris containing titanium protect the surface.

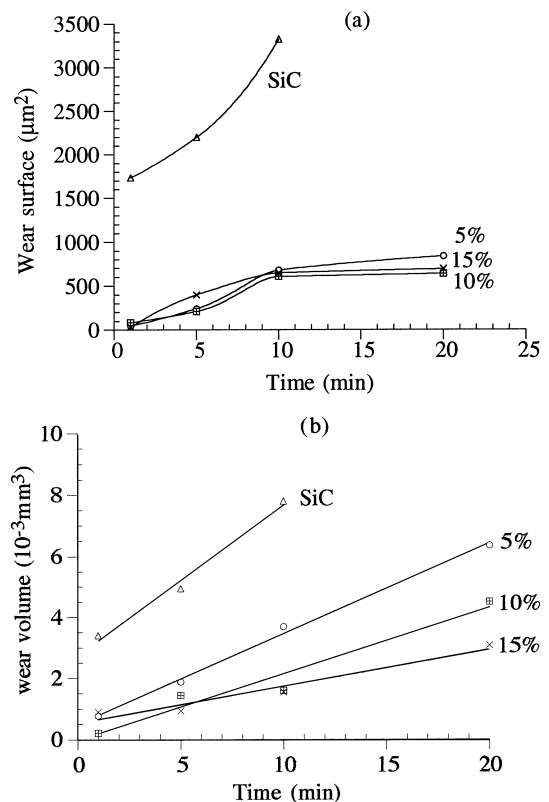


Fig. 16. Wear of SiC flats (a) and composite pins (b) for asymmetrical couples composite pins/SiC flats in water.

In water, the problem is different because debris are eliminated. Composites pins are more resistant to pull out than SiC, that decreases wear of composite pins.

4 Discussion

We consider wear successively in air and then in water.

In air, with 40% relative humidity, it is not possible to classify the materials with regard to their wear resistance: the results depend on the test realised. But, generally, the composite materials behave better than SiC.

However, wear mechanisms have been described.

For composite pins or flats, some grains are pulled out and then ground in the contact. The specific surface of these particles increases during the test, making easier chemical reactions with environment (air). Then, the debris are oxidized: EDS analysis has revealed the systematic presence of oxygen, silicon and titanium in the debris. The quantity of debris is limited and they are amorphous as observed by X-rays. The wear of SiC at elevated temperature (600°C) in air, led to amorphous SiO₂, characterised by XPS.¹³ Unfortunately, ESCA did not allow us to determine the compositions, due to a large contamination. Considering our

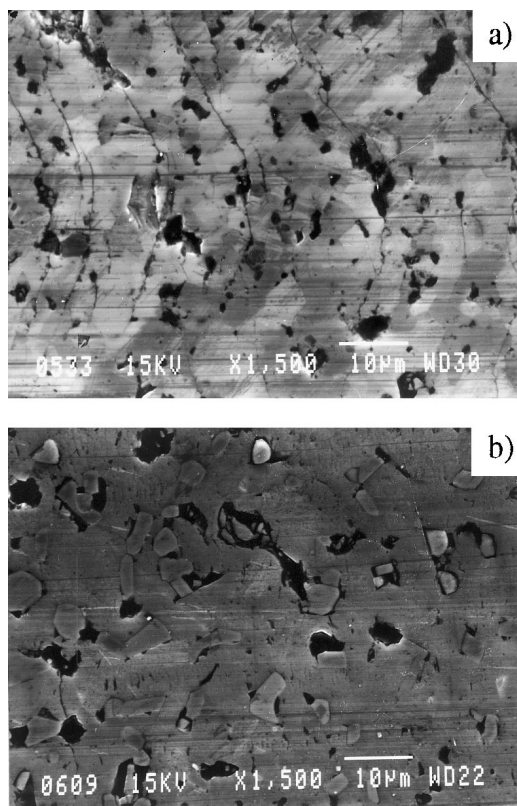


Fig. 17. (a) SiC flat: surface polished with circular cracks (asymmetrical couples composite pins/SiC flats in water). (b) Polishing of composite pins, with chipping of grains.

results, and those in literature, we assume that the particles, issued from composites, have reacted with oxygen in air by tribooxidation, and formed amorphous oxidized phases, at TiO₂, SiO₂ and B₂O₃.

The third body, issued from this tribochemical reaction, is protective for the surface when it forms a thick, dense and adhesive layer. The wear behavior depends on the stability of the third body formed.

Finally, if the third body is eliminated from the interface, the surfaces are without any protection, and the wear is important. Some pull-out of grains appears and the roughness is filled by oxidised debris. The behavior of our composite materials can be summarized by Fig. 18.

For the SiC flats, the initial mechanism of brittle fracture by cleavages leads to two kinds of behavior:

- in the case of a symmetric couple, rollers form (a classical mechanism for SiC). They have a good load carrying capacity for the ball, but, for the flat, because of the opened geometry of contact, the formation and the elimination of rollers is simultaneous, that leads to an important wear.
- in the case of friction against a composite, the layer of debris comes from the SiC flat and seems to be abrasive for the flat.

We can also conclude here that compact composite debris are protective for the surfaces, whereas debris issued from pure SiC have an abrasive nature.

In water, we can classify the materials: in all the cases, composites wear less than SiC. Between the different composites, it seems that when the TiB₂ content increases, the wear decreases, but the difference between the three kinds of materials is low.

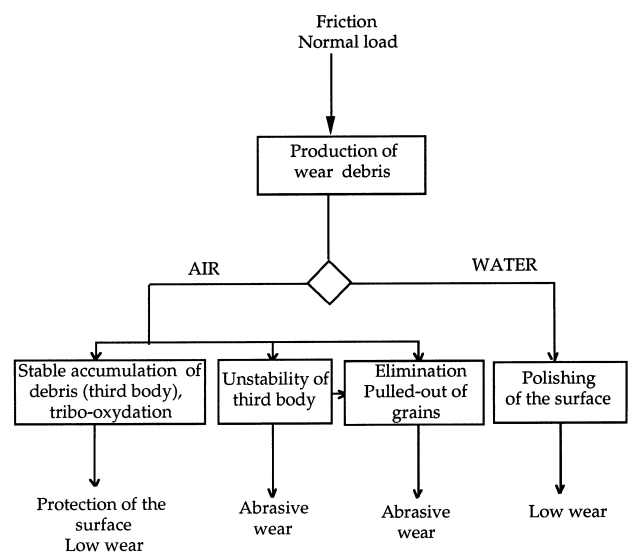


Fig. 18. Wear behavior of SiC/TiB₂ composite materials: a schematic overview.

On the contrary, the influence of water is clear: it decreases by a factor 10 the wear of materials, and by 2 the friction coefficient [Fig. 9 and 12].

The wear mechanisms are very different from those in air:

- the SiC ball wears by fissuration and pull-out of grains, whereas the SiC flats wear by brittle fracture (cleavages). In the two cases, these mechanisms lead to a severe wear.
- the composite pins are grooved and some grains are pulled-out, but wear is limited
- finally, composite flats are polished: the particles pulled-out form with water a kind of polishing suspension. The flats are also grooved, and some circular cracks appear.

We suppose that the influence of TiB₂ on the wear resistance of SiC/TiB₂ composites might be related to tribo-oxidation in water. Unfortunately, no chemical analysis was possible due to the dispersion of the small quantity of debris in water. The layers containing Ti and O decrease the wear of surface⁷: in our composites, the titanium and boron contents are much higher than in industrial SiC, sintered with boron (0.6 wt%) and carbon (2 wt%) additives (balls and flats), this difference might explain the better wear resistance of composites against monolithic SiC. A lubrication can be efficient with tribo-oxidation products or simply with water.

5 Conclusions

The wear behavior of SiC–TiB₂ composites prepared by reactive sintering has been studied using a pin on flat configuration.

It has been shown that wear mechanisms are modified by the presence of TiB₂ (in comparison with SiC/SiC wear).

- In air, the wear of SiC occurs by cleavages and then by rollers formation, whereas there is the formation of a protective dense layer for the composites.

- In water, SiC wears by cleavages, whereas composites are polished.

Acknowledgements

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