JOURNAL OF MATERIALS SCIENCE 21 (1986) 931–935

Sliding friction and wear of structural ceramics

Part 2 *Analysis of room-temperature wear debris*

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Further analysis has been performed on SiC and partially stabilized ZrO_2 specimens employed in a previous study of sliding friction and wear. Wear volumes have been measured, wear debris has been studied by X-ray diffraction and transmission electron microscopy, and comparative X-ray diffraction studies have been performed on worn and unworn surfaces. There is no correlation between the wear during running-in and the steady-state coefficient of friction established by this process. ZrO_2–ZrO_2 friction couples wear much faster than SiC–SiC couples, which in turn wear faster than ZrO_2–SiC couples. In these last couples wear occurs mostly on the ZrO_2 member, but does not measurably promote the tetragonal to monoclinic phase transformation. Adding graphite to SiC reduces the wear of SiC–SiC couples somewhat, but improving their initial surface finish has the opposite effect. All wear debris exhibited a bimodal particle-size distribution, which observation can be rationalized with the wear surface topographies reported previously.

1. Introduction

In a previous paper [1], hereinafter Part 1, an account was given of a study of the unlubricated sliding friction and wear behaviour of various like and unlike combinations of four structural ceramics. The experiments were conducted in air at room temperature under conditions approximating the motion of an automotive piston and cylinder assembly during engine idling. The four materials were sintered α-SiC (α-SiC), siliconized SiC (Si-SiC), graphitized SiC (C-SiC) and a Y_2O_3-stabilized ZrO_2 (PSZ). The phase and chemical constitutions and the microstructures of these materials were reported in Part 1.

Along with the high steady-state coefficients of friction μ_f observed in Part 1 ($0.25 \leqslant \mu_f \leqslant 0.50$), there was considerable generation of wear debris. Samples of that debris were collected at late stages of each test run, and these have now been analysed by X-ray diffraction, transmission electron microscopy and energy-dispersive X-ray spectroscopy. In addition, comparative X-ray diffraction studies have been carried out on the worn and unworn surfaces and estimates have been made of the volumes of the wear scars. This paper reports the results of these various studies and attempts to relate them to the friction data, the profilometry measurements and the scanning electron microscopy studies reported in Part 1.

2. Results

2.1. Volumes of wear scars

An optical microscopic method was used to estimate the total volume of material removed from the larger (lower) member of each friction couple tested in Part 1. First, the microscope was focused on the unworn part of the original surface and its fine-focus drive screw was zeroed. Then, the depth of the wear scar below this reference surface was measured at about 20 widely different locations distributed throughout the scar by reading the scale on the drive screw after re-focusing at each location in turn. Finally, the wear volume was obtained by numerical integration. This approach could not be applied to the smaller (upper) specimens, because the wear scar on such a specimen generally covered its whole surface. Instead, a micrometer was used to measure the thickness before and after wear at between four and nine locations on each specimen, and the wear volume was calculated from the differences between these measurements. This method was less accurate than the optical method. It did, however, have the advantage of not including in the estimated wear volume the extraneous effects of chipping at the leading/trailing edges of these specimens (see Part 1 [1]).

The results obtained are summarized in Table I. Note that in each case it is the total wear volume that is given, regardless of the number of cycles of wear responsible for the loss. No attempt has been made to calculate a wear coefficient [2, 3] (volume removed/normal force × sliding distance) because the friction coefficient – and presumably, therefore, the wear coefficient also – varied in a different manner for each couple as it developed its steady-state wear surface topography. In the case of the like SiC couples there was never more than 50% difference between the volumes of material removed from the smaller and the larger specimens. The Si-SiC–Si-SiC couple exhibited more wear and the C-SiC–C-SiC couple less wear than the equivalently prepared α-SiC–α-SiC couple (II in Table I); and the better-finished α-SiC–α-SiC couples (III and IV) exhibited more wear than did similar couples with initially rougher machined surfaces (I and II). The PSZ–PSZ couple exhibited more wear

0022–2461/86 $03.00 + .12

TABLE I Wear data for different friction couples

Friction couple (Smaller–larger specimen)	Surface finish	Steady-state coefficient of friction	Wear volume (mm^3)		Number of cycles of sliding wear
			Smaller specimen	Larger specimen	
α-SiC–α-SiC	Coarse-machined (I)	0.43	130	150	864 000
α-SiC–α-SiC	Fine-machined (II)	0.31	150	100	576 000
α-SiC–α-SiC	Lapped and polished (III)	0.45	280	290	468 000
α-SiC–α-SiC	Lapped (IV)	0.33	260	160	152 000
C-SiC–C-SiC	Fine-machined	0.25	130	80	468 000
Si-SiC–Si-SiC	Fine-machined	0.33	390	440	468 000
PSZ–PSZ	Fine-machined	0.40	3350	440	468 000
PSZ-α-SiC*	Fine-machined	0.41	120	10	270 000
Si-SiC–C-SiC	Fine-machined	0.43	390	390	468 000
C-SiC–PSZ	Fine-machined	0.50	~0	80	480 000

*Machined perpendicular rather than parallel to the sliding direction.

than any of the like SiC–SiC couples, and in this case ~90% of the wear occurred on the smaller sample. Similarly, when PSZ wore in contact with α-SiC or C-SiC, most of the wear occurred on the PSZ member of the couple, regardless of whether this was the bigger or the smaller specimen. However, the volume lost from PSZ sliding against α-SiC or C-SiC is about an order of magnitude less than the volume lost from PSZ sliding against itself; and these forms of SiC similarly experience an order of magnitude less wear when sliding in contact with PSZ than when sliding on themselves. When Si-SiC slides against C-SiC the amount of material lost is much the same as when Si-SiC slides against itself and considerably greater than the amount lost when C-SiC slides against itself.

2.2. X-Ray diffraction studies

Comparison of the diffraction patterns from the various worn and unworn SiC specimens revealed only one significant feature: the appearance of two additional small peaks corresponding to d spacings of 0.7107 and 0.3566 nm on one worn Si-SiC surface. Subsequent scanning electron microscopy and energy-dispersive X-ray spectroscopy revealed the presence of small particles containing sodium, potassium, aluminium, iron and chlorine on this surface and the C-SiC surface that it was worn against. Evidently this particular friction couple was somehow contaminated by dust particles having a layered silicate structure [4]. There was no evidence in any of the diffraction patterns of the presence of an amorphous SiO_2 layer on any SiC wear surface.

The X-ray diffraction studies of the worn and unworn PSZ specimens and of the wear debris generated from the latter all showed the presence of large amounts of the tetragonal and small amounts of the monoclinic phase, but they provided no clear evidence of the presence of any cubic material. The proportion of the monoclinic to the tetragonal phase appeared to be slightly higher on PSZ surfaces worn against either PSZ or α-SiC than on unworn PSZ surfaces, but the diffraction pattern obtained from the wear debris did not confirm this trend.

2.3. Transmission electron microscopy

The transmission electron microscopy studies revealed that in all cases the wear debris exhibited a bimodal particle-size distribution: some particles were micrometre size and the others ranged in size from 5 to 50 nm. Particles of both sizes had a slightly rounded, equiaxed appearance. Selected-area diffraction studies suggest that all of the particles are single crystals.

Fig. 1 is a low magnification bright-field image of wear debris resulting from the sliding of one diamond-lapped α-SiC surface against another, and Fig. 2 is a high magnification dark-field image of debris created by sliding two lapped and polished α-SiC surfaces together. It is clear from the diffraction contrast, particularly in the dark-field image, that both micrographs show clusters of 5 to 20 nm particles. Despite repeated efforts to use ultrasonic techniques to break up such clusters, it was not possible to disperse the wear particles individually. Nevertheless, it was on occasion possible to obtain single-crystal diffraction patterns from one particle within a cluster. Fig. 3, for example, shows both a ring pattern and a single-crystal pattern obtained from a cluster of wear particles created by sliding Si-SiC on C-SiC. The radii of

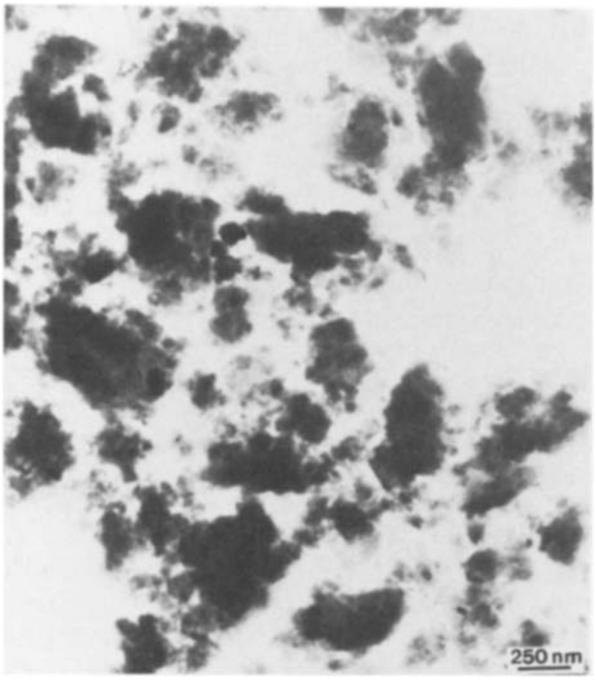

Figure 1 Bright-field transmission electron micrograph showing 5 to 20 nm equiaxed particles produced by the wear of one diamond-lapped α-SiC surface against another.

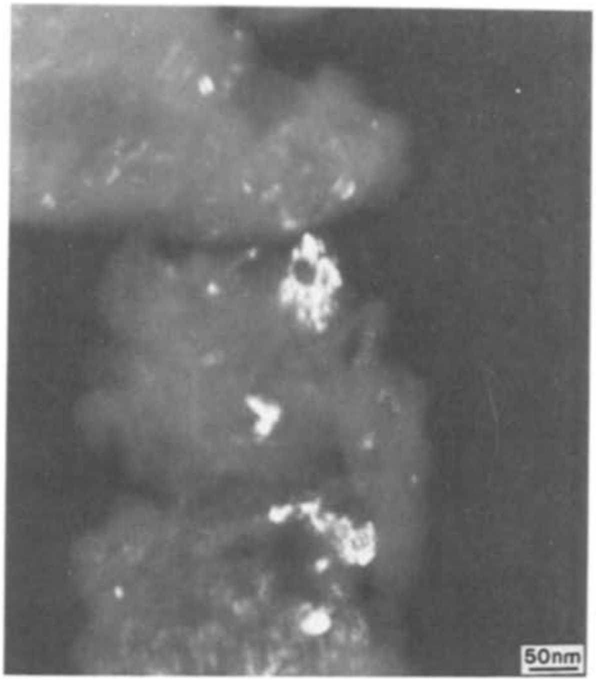

Figure 2 Dark-field transmission electron micrograph showing 5 to 20 nm equiaxed particles produced by the wear of one-diamond lapped and polished α-SiC surface against another.

Figure 4 Bright-field transmission electron micrograph of micrometre size and occasionally smaller particles of tetragonal PSZ produced by the wear of fine-machined PSZ against similarly machined C-SiC.

the diffraction rings are consistent with one or more of the $\{10\bar{1}3\}$ and $\{20\bar{2}4\}$ d spacings of the 6H polytype of α-SiC, the $\{10\bar{1}2\}$, $\{10\bar{1}3\}$, $\{20\bar{2}0\}$ and $\{0004\}$ d spacings of the 4H polytype of α-SiC, and the $\{220\}$ and $\{400\}$ d spacings of silicon; and the dense rows of spots in the single-crystal pattern are consistent with a 1.4 nm (near $\{0001\}$) $\{h0\bar{h}l\}$ d spacing of the 6H polytype of α-SiC. 6H and 4H are two of the three most dominant polytypes in Acheson process SiC [5], and silicon comprises 41 wt % of Si-SiC [1].

Figs. 4 and 5 show, respectively, micrometre size and 5 to 50 nm size PSZ wear particles. The former were generated by sliding PSZ against C-SiC and the latter by sliding PSZ against itself. The selected-area diffraction pattern obtained from the particles shown in Fig. 5 is presented in Fig. 6. The radii of the diffraction rings are consistent with the $\{111\}$, $\{200\}$, $\{202\}$, $\{131\}$ and $\{222\}$ d spacings of tetragonal ZrO_2, confirming the X-ray finding that the particles

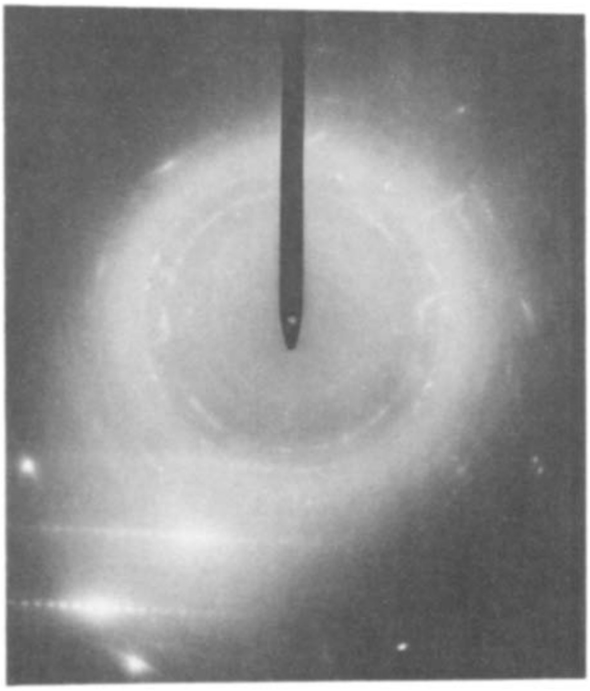

Figure 3 Selected-area diffraction pattern from particles produced by wearing one fine-machined Si-SiC surface against another. The ring pattern derives from silicon and the 6H and 4H polytypes of α-SiC. The dense rows of spots in the single-crystal pattern also come from the 6H polytype of α-SiC. They are consistent with an $\{h0\bar{h}l\}$ d spacing only slightly smaller than the $\{0001\}$ d spacing.

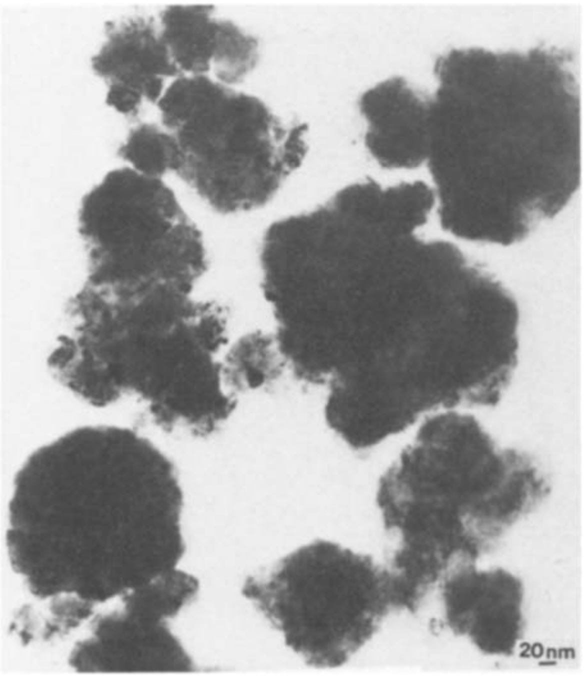

Figure 5 Bright-field transmission electron micrograph showing 5 to 50 nm particles of tetragonal PSZ produced by wearing one fine-machined PSZ surface against another.

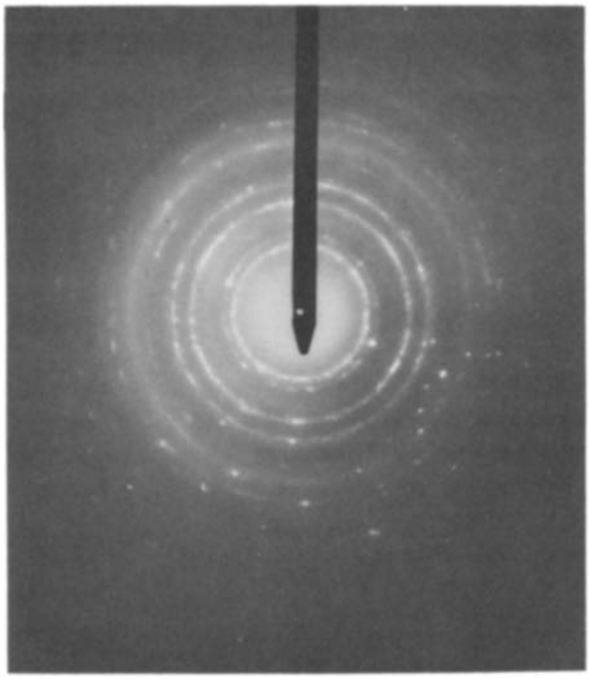

Figure 6 Selected-area diffraction pattern from the particles shown in Fig. 5. The ring pattern identifies the particles as tetragonal.

are almost exclusively tetragonal. A combination of similar analysis and energy-dispersive X-ray spectroscopy of the micrometre size particles shown in Fig. 4 reveals that these also are exclusively tetragonal PSZ. As would be expected from the low wear of C-SiC against PSZ, neither carbon nor SiC could be detected in this debris.

3. Discussion

Because wear volume was measured only at the end of each friction experiment rather than at intervals during the experiment, it is not possible to determine from the present data whether the variations in coefficient of friction observed during the running-in of the friction couples are accompanied by variations in wear coefficient. The data do, however, show that there is no correlation between the steady-state coefficient of friction and the total loss of material during and (in terms of engine operation) shortly after running-in. Despite the different numbers of cycles of wear experienced by different friction couples, the present data also permit a broad distinction to be made between the wear behaviour of PSZ–PSZ, SiC–SiC and PSZ–SiC couples. For PSZ–PSZ couples the total wear volume was up to an order of magnitude larger than for SiC–SiC couples. The same result has also been obtained in unidirectional sliding wear tests of similar couples in air at room temperature [6]. Unlike PSZ–SiC couples concentrate the wear on the PSZ member, but nevertheless produce a significant (at least two- or three-fold) reduction in total wear volume as compared to SiC–SiC couples. Further, the SiC member of an unlike PSZ–SiC couple experiences very little wear.

Comparison of the wear behaviour of like α-SiC–α-SiC, C-SiC–C-SiC and Si-SiC–Si-SiC frictional couples leads to three conclusions. First, a better initial surface finish leads to greater loss of material during and shortly after running-in. Second, the Si-SiC material wears more during this period than either α-SiC or C-SiC. And third, the presence of even a small quantity of free carbon (graphite) does have a beneficial effect on the wear behaviour of SiC. It would therefore seem worth while exploring the tribological behaviour of other C-SiC composites containing greater quantities of graphite.

The wear behaviour of the unlike friction couples is more difficult to explain. In the case of Si-SiC–C-SiC, the beneficial effect of graphite reported above did not carry over, perhaps because the graphite content of the C-SiC was too low. It may also be significant that α-SiC, which contains only one third to one half as much graphite as C-SiC, wears only slightly more than C-SiC when it slides in contact with PSZ. This suggests that the low wear of both forms of SiC in this situation derives from the presence of copious PSZ wear debris between the sliding surfaces rather than from any solid-state lubricating effect of graphite. Further support for this argument comes from the observation that in both PSZ–SiC couples upwards of 90% of the total wear occurred on the PSZ member, regardless of whether this was larger or smaller than the SiC member. SiC is considerably harder than PSZ (Vickers Hardness ~ 33 GPa compared with ~ 12 GPa at loads of $\lesssim 1$ kgf [1]), and so PSZ wear debris trapped between an SiC surface and a PSZ surface might reasonably be expected to abrade the latter more than the former.

The X-ray and electron diffraction studies did not demonstrate conclusively whether the contact stresses generated during sliding caused any tetragonal PSZ to transform martensitically to the monoclinic polymorph. On the one hand the X-ray diffraction patterns obtained from the specimen surfaces indicated a slight increase in the monoclinic to tetragonal ratio after wear; but on the other hand both the X-ray and the electron diffraction studies of the wear debris failed to reveal the presence of any monoclinic material. Nor have the efforts of other investigators succeeded in defining clearly the effect of contact stresses on the near-surface phase composition of Y_2O_3-stabilized ZrO_2. Thus, Gupta *et al.* [7] found that comminution did indeed induce the tetragonal to monoclinic transformation in "low" Y_2O_3-content forms of ZrO_2 initially containing a high percentage of the tetragonal phase, and Mitsuhashi *et al.* [8] observed the same phenomenon in pure ZrO_2. In contrast, Reed and Lejus [9] and Hasegawa [10] found that various grinding and abrasive processes did not affect the tetragonal constituent of diphasic (cubic plus tetragonal) Y_2O_3-stabilized ZrO_2, but instead partly converted the cubic constituent to either the tetragonal or a rhombohedral form, respectively.

Perhaps the most surprising finding to emerge from the transmission electron microscopy studies of the wear debris from both SiC and PSZ specimens is the bimodal nature of the debris particle size distribution. Though all of the particles have the same rounded, equiaxed shape, some are micrometre size while others are measured in tens of nanometres; and there appear to be relatively few particles of intermediate (few hundred nanometre) size. In the case of the SiC materials, it is suggested that the fine particles are the product of the "polishing" and "grooving" processes described in Part 1 [1] and that the micrometre size particles are the product of the "microchipping" process reported in Part 1. If this hypothesis is correct, the similarity in shape of the two sizes of particles suggests that "polishing" and "grooving" occur by very fine-scale brittle fracture rather than by plastic flow (i.e. dislocation glide). Additional support for this contention is provided by the lack of evidence of dislocations in the wear particles. The lack of intermediate-size debris particles suggests further than the micrometre size particles do not undergo extensive comminution between the opposing sliding surfaces during whatever period of time elapses between their formation and their expulsion from the sliding interface.

Since the PSZ wear surfaces described in Part 1 do not exhibit two topographically different sorts of regions wherein obviously different wear processes were operative, the bimodal debris particle size distribution observed in the present work must have a different origin. Since the larger wear particles are comparable in size with the constituent grains, it is suggested that they are the result of intergranular fracture processes (i.e. grain "pull-out"); and it is further suggested that the smaller wear particles are the result of intragranular fracture processes (i.e. the chipping way of part of a grain exposed at the wear surface).

In this view, the broad difference in wear behaviour between PSZ and SiC stems, at least in part, from a postulated difference in the relative ease of inter- and intra-granular fracture between the two materials. It is suggested that intergranular fracture is relatively more difficult in SiC, with the result that grains tend to pull out from this material but rarely, and then only after most of their volume has been removed by very fine-scale chipping. This latter process leads to "polishing" in regions where pull-out chances not to occur. When pull-out does occur, however, it is suggested that it is autocatalytic, promoting further pull-out and larger-scale chipping in the immediate vicinity of the original event and thereby creating a contiguous area in which wear occurs by microchipping. In PSZ, in contrast, it is envisaged that intergranular fracture is relatively easier (or intragranular fracture relatively more difficult). As a result the rougher wear surface observed in Part 1 develops. The overall topography of this surface is determined by the process of grain pull-out, and there is never enough very fine-scale chipping to permit "polishing".

Acknowledgement

This work was supported by Sohio Engineered Materials Company.

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Received 11 April
and accepted 21 May 1985