JOURNAL OF MATERIALS SCIENCE **22** (1987) 3917–3923

Characterizing the surface contact behaviour of ceramics

Part 2 *Chemo-mechanical effects*

J. T. CZERNUSZKA*, T. F. PAGE‡
Department of Metallurgy and Materials Science, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

The effect of chemical environment (a homologous series of *n*-alcohols) on the near-surface hardness and wear behaviour of two glass-bonded ceramics has been investigated. A change by upto a factor of two in both these parameters may be observed, with a good correlation between them. The indentation fracture behaviour of one material was also studied, and the environmental dependence of crack length suggests a slow crack-growth mechanism. The results show that the near-surface mechanical properties of ceramics may be modified by environmental means.

1. Introduction

Indentation hardness is often used as a material's selection parameter for inferring wear resistance. However, Part 1 [1] suggested a number of reasons why this correlation should not generally hold and demonstrated the variation of hardness (and thus materials ranking order) with both indentation size and temperature for a number of ceramics. It was also established there that environment might play a sensitive role in determining the apparent hardness of a surface. This effect has been the impetus for the present investigation. A previous paper [2] has established the effect of water on the low-load hardness of two alumina-based materials. By contrast, the aim of the present study has been to examine systematically the effect of an essentially non-corrosive chemical environment (a series of *n*-alcohols) on the near-surface hardness and wear response of one alumina-based and one titania-based glass-bonded ceramics. The localized indentation fracture of the titania-based ceramic has also been investigated utilizing the same environments and an attempt made at correlating the observed behaviour.

2. Environmental effects on hardness, fracture and wear

While the following section briefly describes various environmental effects on the surface contact response of ceramics, more extensive reviews may be found in the literature (e.g. [3–5]).

For some time it has been widely observed and recognized that the near-surface plasticity of ionically and covalently bonded materials (as revealed by hardness tests, for example) is markedly dependent on the chemical environment in which they are indented [6]. Such variations under non-corrosive chemical environments are termed "chemo-mechanical effects". These effects are distinct from the environmental effects on fracture appearing as slow crack growth, etc., (e.g. [7]). A range of mechanisms for chemo-mechanical effects have been suggested, including chemi-sorption-induced reductions in surface free energy [6], changes in the electronic state of near-surface point defects and dislocations manifested as variations in their mutual interactions [8, 9] and near-surface band bending effects [10, 11]. More recently, it has been suggested that only charged kinks on dislocations are influenced by surface effects [12], as well as a "hydrogen embrittlement" mechanism [13], whereby protons diffuse into the surface from the environment. Also, charge and deformation-induced bending of the energy levels around dislocations [10, 11, 14], and a recombination-enhanced defect mobility [15] have been invoked to explain the possibly related photo-mechanical and electro-mechanical effects. Of course, any combination(s) of the above mechanisms may operate in practice.

With regard to wear, environmental effects on the drilling behaviour of ceramics and rocks have also been reviewed [4, 5]. For example, large variations in wear rate have been obtained in MgO [16], glass [17], granite [18] and alumina [19]. In general, the mechanisms accounting for this behaviour relate to environments which cause a decrease in plastic flow (i.e. an increase in hardness) and so brittle fracture becomes more dominant during cutting, hence, resulting in higher wear rates. It has been suggested, however, that the primary factor responsible for variations in hard rock drilling efficiency in the environmental sensitivity of wear of the cutting tool (i.e. diamond) [4]. When the hardness of the rock is at a maximum, the friction should be at a minimum and so the tool runs cooler;

---

[*] *Present address*: Department of Metallurgy and Science of Materials, University of Oxford, Parks Road, Oxford, UK.
[‡] *Present address*: Department of Metallurgy and Engineering Materials, University of Newcastle Upon Tyne, Newcastle Upon Tyne, NE1 7RU, UK.

0022–2461/87 $03.00 + .12

reduced temperatures lead to less oxidation. Also, the influence of additives on the rheological properties of the suspension of rock cuttings should not be ignored. For example, it could be that if a surfactant significantly altered the viscosity of the slurry around the drill bit, cooling could be much improved. It seems, therefore, that in addition to mechanisms applicable during quasi-static hardness tests, other, lubrication dependent properties may also be important in explaining chemo-mechanical effects during wear.

The purpose of this paper, however, is not to discriminate between these (or possibly other) mechanisms, but to show the magnitude of the environmental effects in relation to the hardness, fracture and wear behaviour of two commonly used technical ceramics.

3. Experimental procedure

3.1. Materials and preparation

Two commercially available de-based ceramics were chosen for this study, namely a ~87% alumina (RG) and a ~93% titania (TE), with the balance being an amorphous silica phase binding the grains. Microstructural and microanalytical data for these specimens together with details of the polishing methods used are given in Part 1 [1]. Back-scattered electron (BSE) imaging in the scanning electron microscope (SEM) proved ideal in delineating the grains from the binder phase by atomic number contrast (e.g. [20]). Examples of such images are shown in Figs 1a and b. The grain size is typically ~5 μm for RG and ~1.5 μm for TE.

3.2. Indentation testing

The polished specimens were heated to 500° C in air for approximately 6 h in an attempt to remove the physi-sorbed and chemi-sorbed water (e.g. [21, 22]) and then quenched into the required liquid environment – one of a series of homologous *n*-alcohols. These environments were chosen both because *n*-alcohols have been reported as inducing significant chemo-mechanical effects in alumina [18, 19] and to allow our results to be compared with this earlier work. A Knoop profile indentor (on a Leitz Miniload microhardness tester) was used at a load of 10 g to provide still visible impressions at the low penetrations necessary for investigating environmental effects. In this case, indentations were typically 10 μm long and 0.3 μm deep. A constant indentor dwell time of 15 sec was chosen to avoid anomalous indentation creep effects [21]. SEM examination of the resultant indentations was necessary to improve the accuracy of the measurements. To improve contrast, surfaces were tilted through 45°, the tilt axis being aligned with the long axis of the indentations so as to prevent their fore-shortening. Fig. 2 plots the results of an average of 10 to 15 measurements made under each condition. For these measurements, indentations tended to span a few grains and some of the glassy phase. Indentations intersecting surface pores were excluded. Also, care was taken to use liquids only from freshly opened bottles and to check that hardness values in each liquid did not vary within the time of the experiments (i.e. no degradation of the environments was observed). For comparison, indentations were also made *in vacuo*, after prior heating to 500° C *in vacuo*. Details of this machine are given in [23].

In addition to the above experiments, and because TE exhibited a well-defined median/radial crack geometry when indented with a Vickers profile indentor at loads of 500 g and above, the variation of radial crack length with environment was also investigated. The results from 1 kg indentations (for which the crack span was much greater than the indentation diagonal) are plotted in Fig. 3.

3.3. Wear experiments

The wear rig was a modified metallographic polishing machine, a schematic diagram of which is shown in Fig. 4. The load arm was fixed 80 mm from the centre of an aluminium lap rotating at 170 r.p.m., equivalent to linear velocity at 1.4 m sec^{-1}. A normal load of 1 kg was maintained throughout. Three parallel sided discs of the sample materials (3 mm thick) were sectioned from bars and held in an equilateral triangular configuration in a brass jig. This arrangement was chosen for mechanical stability and as a compromise between contact pressure (decreasing with more samples) and the necessity of ensuring that all the specimens were moving at approximately the same speed (more difficult with more specimens per holder).

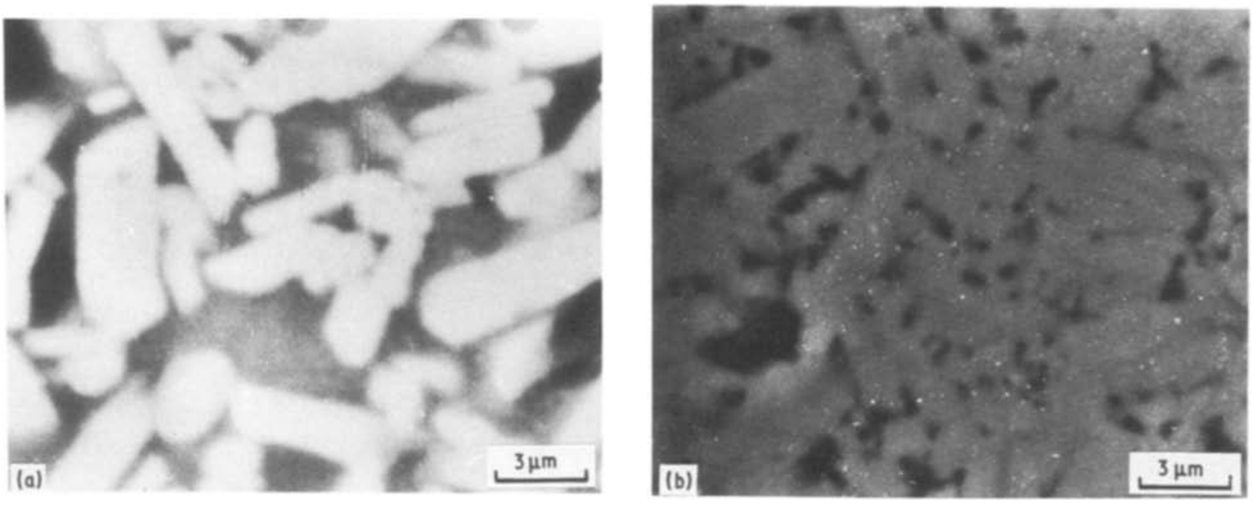

Figure 1 BSE images of (a) RG and (b) TE.

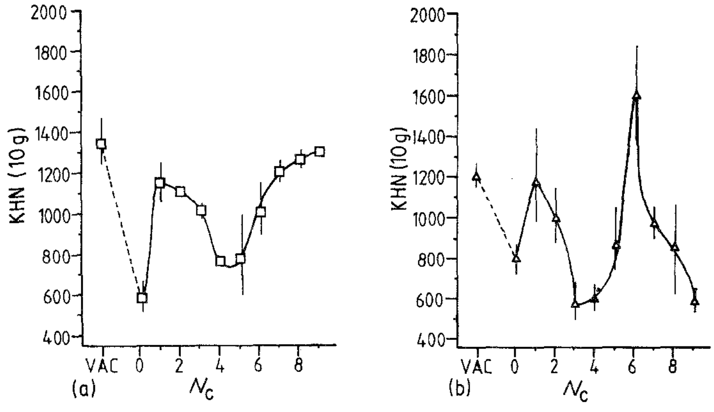

Figure 2 Plot of Knoop hardness against the alkyl chain length in an *n*-alcohol (N_c). Also included are values obtained by indenting under water ($N_c = 0$) and under vacuum. (a) RG and (b) TE.

The aluminium lap had a 3 mm deep channel cut into it to retain the liquid and to ensure that the specimens were completely immersed. Fresh 6 μm diamond paste was added every 30 sec. Wear rates were determined from thickness measurements and are presented in Fig. 5 as an average of at least three trials. Separate samples were used for each run and each environment for subsequent microscopical examination. In each case samples were briefly "run-in" before the tests were started.

4. Results

4.1. Indentation plasticity

For the alumina-based material (RG), Fig. 2a, the Knoop hardness was found to vary with N_c (the number of carbon atoms in the alkyl group) with hardness maxima corresponding to methanol and nonanol, and minima at butanol and pentanol. A pronounced increase in hardness is observed on going from water to methanol, followed by a slow decline to butanol and pentanol, whereupon the hardness increases again. For the titania-based material (TE), Fig. 2b, Knoop hardness was again found to vary with N_c, but this time exhibiting hardness maxima at methanol, hexanol and nonanol, and minima for propanol and heptanol. The behaviour of each material is quite unique and, for each, it is possible to obtain at least a two-fold change in hardness between maxima and minima. However, in all cases the maxima observed are slightly less than under vacuum, but considerably more than under water ($N_c = 0$) or water-containing environments.

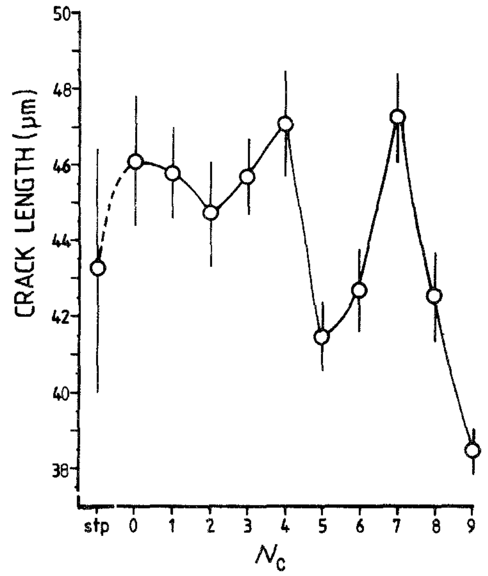

Figure 3 Plot of crack length, *c*, against N_c. The cracks were introduced by a 1 kg load Vickers indentation.

Hardness values at loads of 1 kg (Vickers indentor, penetration ~ 6 μm) were found to be independent of environment (within experimental scatter) confirming the surface specificity of the effect.

4.2. Indentation fracture

The radial crack length measurements are presented in Fig. 3 and show a similarly pronounced effect of environment. In this case, sharp minima correspond to pentanol and nonanol with a slight dip for ethanol; maxima occur at methanol, butanol and pentanol. There is an absolute variation of ~ 8.5 μm depending on environment.

4.3. Wear experiments

The results of the wear experiments are presented in Fig. 5 and again exhibit a marked environmental influence. For RG, the wear rate is a maximum when it is abraded under water and butanol. TE also possesses a maximum at butanol, but lesser ones at water and heptanol, and pronounced minima at ethanol and hexanol. These environmental influences are sufficient to cause the relative wear rates of RG and TE to interchange. For example, under water TE has the higher wear rate and the lower under hexanol.

5. Discussion

5.1. Environmental effects on hardness

Previous studies of environmental effects on single-crystal sapphire [18] showed that hardness maxima

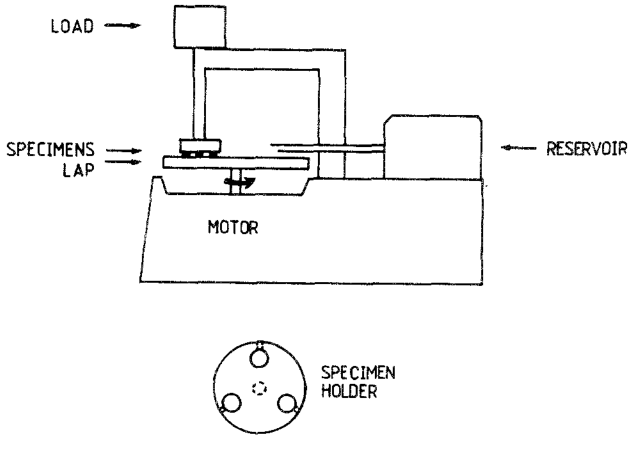

Figure 4 Schematic diagram of the wear apparatus.

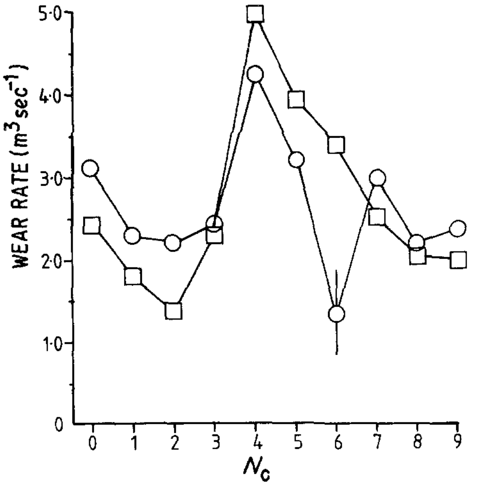

Figure 5 Plots of wear rate against N_c. (○) TE, (□) RG.

were obtained for tests made under pentanol and nonanol. These are not the same environments which caused maxima in hardness for the alumina-based material used in this study (RG). Further work, however [19], showed that the positions of these maxima with respect to the environment could be altered if polycrystalline aluminas were used. This was explained in terms of the different impurities present in these samples. Bearing this in mind, it is almost certain that the impurities in RG would be different still and indeed a dependence of environmental effects on differing impurities in MgO has been reported [9]. Thus, there is a clearly established need to assess environmental effects in specific environment/materials couples.

Because this paper presents the first published results of an environmental effect in a titania-based ceramic we cannot compare our data with any previous work.

In both cases, polycrystalline samples have been consciously chosen for study in order to explore the magnitude of any chemo-mechanical effects on hardness in these ceramics in the form in which they would be used in various wear-resistant applications. Thus, we have been unable to explore the crystallographic anisotropy of these effects though such sensitivity might be expected depending on the slip system activated during indentation (see, for example, [11, 19]).

The time lapse between making indentations in each environment and measuring them in either air or vacuum (SEM) is believed to have no effect on the results.

5.2. Environmental effects on indentation fracture

The crack length measurements for TE (Fig. 3) are markedly dependent on environment, whereas the Vickers hardness values at loads of 1 kg are constant within experimental scatter. Because the development of the radial crack system is generally controlled by nucleation during loading coupled with crack extension from the residual stresses on unloading, it would be expected that the large plastic zones associated with lower hardness values would result in larger cracks. This effect has been clearly demonstrated during the temperature-variant hardness testing of ceramics [23], but no such correlation was observed here. Further, if crack initiation was facilitated by the interaction of dislocation slip, as in MgO [16], then it would also be expected that the curves of Figs 2b and 3 should be mirror images, i.e. a low hardness should again coincide with a large crack extent. If, on the other hand, blunting of the crack tips by dislocation activity itself facilitated by environmental factors occurs, then the curves should coincide. That is, a low hardness now implies a short crack extent. It is evident that none of these explanations hold. However, a "stress-corrosion" mechanism has been proposed to explain the environmentally sensitive crack propagation of glass [7], and such slow crack-growth phenomena have been well-documented in ceramics. It could well be the case for TE that on unloading, the radial cracks undergo environmentally assisted slow crack growth. Fig. 6 shows such an indentation-induced crack in TE where the crack path is through both the glass and grains. Thus, slow crack growth through either, or both, phases may be responsible. However, to counter this argument, the cracks did not appear to extend further even when left immersed in the liquid for a few minutes after indentation. Observation was always within a few minutes of indentation. Thus, while the effect of environment on crack extent is obviously involved, the actual mechanism(s) are still uncertain.

5.3. Environmental effects on wear

To determine the mode of deformation of the worn ceramic surfaces, SEM examination was performed.

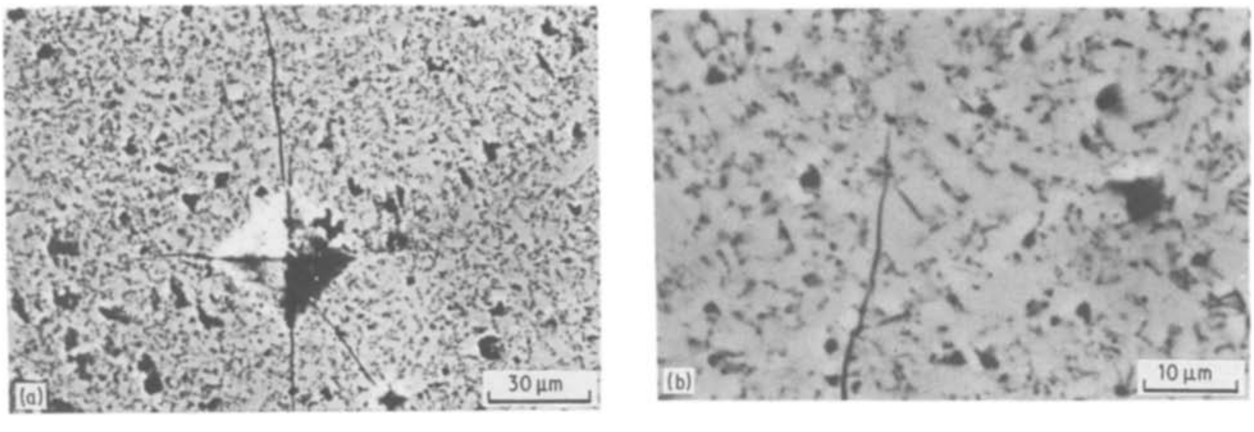

Figure 6 1 kg load Vickers indentation in TE. (a) SE mode and (b) magnified view of a portion of a crack in the BSE mode (see text).

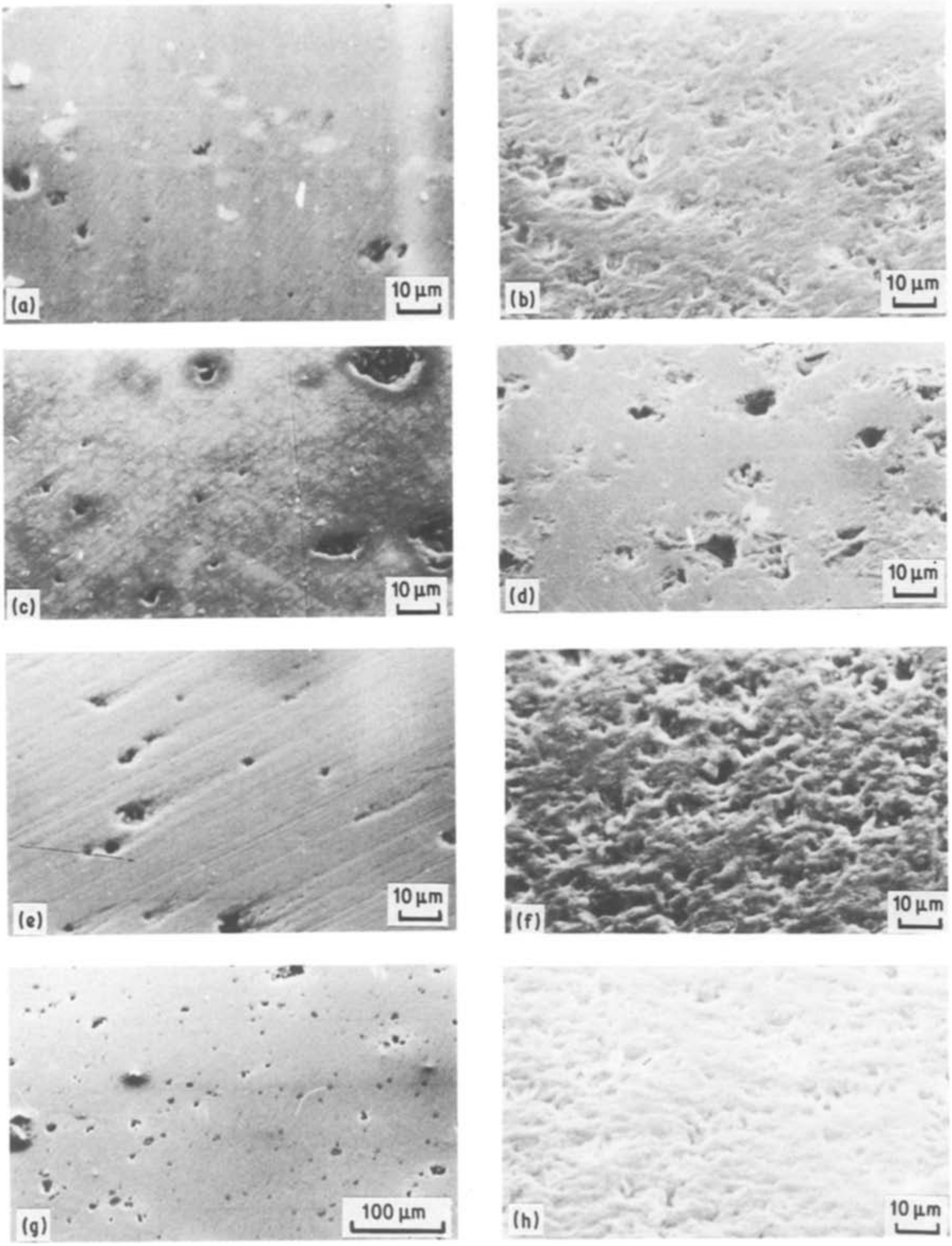

Figure 7 SE mode images of surfaces worn under various environments: (a) and (b) under water, (c) and (d) methanol, (e) and (f) butanol, (g) and (h) hexanol, for TE and RG, respectively. All images tilted 45° towards the detector.

Representative micrographs are presented in Fig. 7. For TE, it is apparent that the surfaces contain mainly plastically deformed scratches. Pits, characteristic of brittle fracture, were occasionally observed. In this respect, the TE surfaces appeared very similar irrespective of the chemical environment in which they were abraded. The RG surfaces, meanwhile, generally contained numerous small pits, of the order of the grain size, suggesting that some individual grain fracture was occurring under the load conditions used. However, on the prominent grains fine-scale grooves may be observed. The surfaces worn under water, butanol and hexanol are all similar, but that worn under methanol has a much smoother appearance with large isolated pits. The shallow depth of the scratches on all surfaces suggests that they should be environmentally affected.

For metals, for which plasticity-dominated wear is the rule rather than the exception, wear rates generally follow an inverse relationship to hardness. If such a relationship holds for ceramics wearing predominantly by a plasticity mechanism (i.e. exhibiting fine ploughed grooves, rather than fracture), then a similar relationship may hold. In this case though, rather than

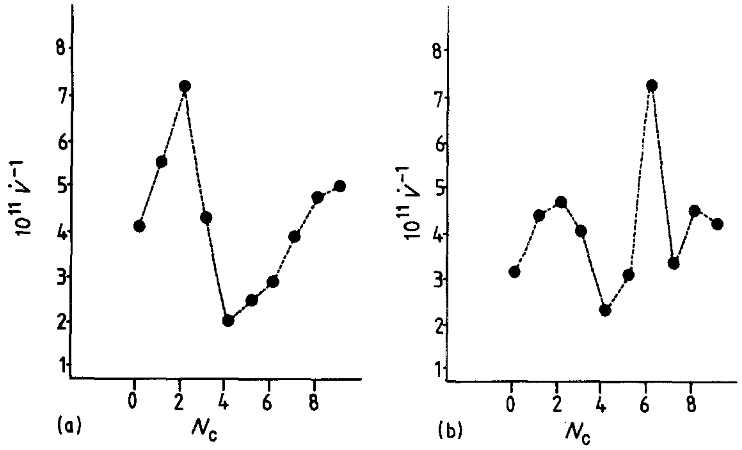

Figure 8 Plot of wear resistance against N_c. (a) RG and (b) TE.

using a single macrohardness value, it is thought better to choose a hardness value the scale of which is commensurate with that of the scratches. That is, the environmentally dependent hardness values of Fig. 2 should be compared with the wear rates. In fact, it is easier to compare hardness values against wear resistance (the reciprocal of wear rate) and these are plotted in Fig. 8. The agreement between Figs 2 and 8 is encouraging but not exact, in that only for alcohols higher than propanol ($N_c = 3$) is there any qualitative agreement.

In order to determine further the reasons for the wear : environment behaviour, it is necessary to consider at least three possible sources of control: (1) possible environmental or chemical effects on the abrasive; (2) lubricating effects of the environment; (3) chemo-mechanical effects on the work-piece. Because fresh diamond abrasive was added at regular, and relatively short, intervals, the effects of environment on their efficiency (e.g. cracking, blunting, oxidation, etc.) is unlikely to be of major importance. However, if the environment is affecting material flow beneath the impinging abrasive particles, then a direct correspondence between Figs 2 and 8 should be expected. This, therefore, appears to be the dominant effect and there may be several reasons why the agreement is not exact, including: (1) a time dependent absorption parameter [5]; (2) modification of the chemical environment by the proprietary paste containing the abrasive; (3) temperature effects. The first effect is supposedly due to surface-active molecules having insufficient time to arrive at the freshly created surface before it is subjected to another abrasive action or, even if they do arrive, there may be insufficient time for them to be adsorbed and interact with the surface. This "dynamic shift" [5] is not thought to be applicable to the present circumstances because of the relatively low sliding velocities. Indeed, it should be more noticeable for the longer chain molecules because of steric effects and the observed discrepancy is towards the lower molecular masses. Influence (2) was not investigated but the amount of contamination of the alcohols by the diamond-containing paste should make such effects negligible. The principal effect believed to be involved in (3) is local heating reducing the adsorption of the volatile alcohols. This effect would be more noticeable for the short-chain molecules as observed.

To estimate the heat rise during wear, a hole was ultrasonically drilled from the reverse side of a RG sample to within ~ 500 μm of the wearing surface, into which a Ni/Cr thermocouple was placed. The temperature was continuously monitored and the maximum value achieved was only about 5° C even when the specimen was worn to expose the thermocouple. This temperature rise is certainly a lower bound value. Any temperature rise would be higher at asperities and would clearly effect the adsorption of the lower alcohols to a greater extent than the higher ones. Thus, it seems likely that this effect must be superimposed on the chemo-mechanical hardness plot to provide the correct environment : wear relationship. In passing, if the wear of TE had been brittle fracture dominated (as in, for example, grinding), a closer relationship between Figs 3 and 5 might be expected.

6. Conclusions

It has been demonstrated that the near-surface indentation plasticity and wear rates of two technical ceramics are markedly dependent on environmental factors when exposed to a series of homologous *n*-alcohols. The extent of radial fracture with environment for TE has also been investigated and has also been found to be environmentally sensitive. Large variations in all these parameters have been observed. However, positions of hardness maxima and minima, for the alumina-based material, do not follow published values on single and polycrystalline aluminas and are probably sensitive to both detailed microstructure and impurities. The observations on the titania-based ceramic are new and cannot be correlated with previous work.

The indentation fracture results do not follow the hardness results and may be controlled by slow crack growth.

Microscopy has shown that the wear behaviour of both materials is predominantly in the plasticity dominated regime. However, wear rates do not correlate exactly with the inverse of indentation hardness results, though an encouraging similarity has been observed. Reasons for this discrepancy have been discussed and, because both materials are affected in a similar manner, may possibly arise from localized heating affecting adsorption.

Acknowledgements

The authors would like to thank Professor R. W. K.

Honeycombe FRS, FEng. for the provision of laboratory facilities. J.T.C. acknowledges financial support from SERC under the CASE scheme with ICI (Fibres) Harrogate.

References

1. J. T. CZERNUSZKA and T. F. PAGE, *J. Mater. Sci.* **22** (1987) 3527–36.
2. *Idem, Proc. Brit. Ceram. Soc.* **34** (1984) 981.
3. N. H. MACMILLAN, in "Surface Effects in Crystal Plasticity" (Noordhof, Leyden, 1977) p. 629.
4. G. A. COOPER, in "The Science of Ceramic Machining and Surface Finishing 2", NBS Special Publication 562 (1979) p. 115.
5. A. R. C. WESTWOOD, J. S. AHEARN and J. J. MILLS, *Colloid Surf.* **2** (1981) 1.
6. P. A. REBINDER, Proceedings 6th Physics Conference (State Press, Moscow, 1928) p. 29.
7. W. S. HILLIG and R. J. CHARLES, in "High Strength Materials" (Wiley, New York, 1965) p. 682.
8. A. R. C. WESTWOOD, D. L. GOLDHEIM and R. G. LYE, *Philos. Mag.* **16** (1967) 505.
9. *Idem, ibid.* **17** (1968) 951.
10. J. S. AHEARN, J. J. MILLS and A. R. C. WESTWOOD, *J. Appl. Phys.* **49** (1978) 96.
11. *Idem, ibid.* **49** (1978) 614.
12. W. SCHROTER and P. HAASEN, in "Surface Effects in Crystal Plasticity" (Noordhof, Leyden, 1977) p. 681.
13. R. E. CUTHRELL, *J. Mater. Sci.* **14** (1978) 612.
14. V. F. PETRENKO and R. W. WHITWORTH, *Philos. Mag.* **A41** (1980) 681.
15. J. D. WEEKS, J. C. TULLY and L. C. KIMMERLING, *Phys. Rev.* **B12** (1975) 3286.
16. A. R. C. WESTWOOD and D. L. GOLDHEIM, *J. Am. Ceram. Soc.* **53** (1970) 149.
17. A. R. C. WESTWOOD and R. M. LATANISION, in "Science of Ceramic Machining and Surface Finishing", NBS Special Publication 348 (1972) p. 141.
18. A. R. C. WESTWOOD, N. H. MACMILLAN and R. S. KALYONCU, *J. Am. Ceram. Soc.* **56** (1973) 258.
19. *Idem, Trans. SME/AIME* **256** (1974) 106.
20. J. T. CZERNUSZKA and T. F. PAGE, *J. Microscopy* **140** (1985) 159.
21. J. H. WESTBROOK and P. J. JORGENSEN, *Trans. AIME* **233** (1965) 271.
22. D. A. GRIFFITHS and D. W. FUERSTENAU, *J. Coll. Interface Sci.* **80** (1981) 271.
23. M. G. S. NAYLOR and T. F. PAGE, ELSI V, Proceedings Vth International Conference of Erosion by Liquid and Solid Impact (Cavendish Laboratory, Cambridge, 1979) Paper 32.

Received 24 October 1986
and accepted 22 January 1987