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Chemiomechanical effects on crack propagation: polycrystalline α-Al_2O_3

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The role of environment on microcracks in Al_2O_3 is important as the material has applications in the biomedical field, such as artificial bones. The indentation method of producing radial cracks and measuring hardness is good in that it is reproducible. The radial crack lengths in α-Al_2O_3 are found to be sensitive towards the environment, and the load applied on the indentor. Long-time Vickers' microhardness and radial crack-length measurements in the presence of bio-simulating, aqueous and non-aqueous environments on the surface of α-Al_2O_3 are analysed. In each environment considered, the crack propagation showed a linear variation with the applied load, and the microhardness decreased similarly with time. Evidence was sought to show that the presence of water in bio-simulating liquid helps crack propagation under load. The results are explained in terms of possible interactions between the molecules of Al_2O_3 and the chemical environment and surface energies in the presence of that environment.

1. Introduction

New and promising technologies which require fibre-optic networks, ceramic bone replacements or novel optical and electronic components have placed a high premium on ceramics which will prove particularly resistant to cracking. Indentation analysis [1–3] is a powerful tool for evaluating and characterizing the deformation and fracture properties of ceramic materials, quantified by crack propagation hardness and fracture toughness [4–6]. The basic concept behind indentation testing is attractive in its applications and reproducibility. Intense stress concentration beneath the indentor contact with the surface of the sample causes the material to undergo both reversible and irreversible deformation. The most obvious manifestation of the latter component is the residual hardness impression. The irreversible component is also responsible for any attendant crack initiation [7–9], and the residual stresses can continue to exert a strong influence on crack propagation well beyond the near contact zone [2, 3, 10, 11].

Furthermore, crack propagation and microhardness are shown to be influenced by the environment [12–15]. Several papers [16–25] have reported that the hardness of oxides such as silicate glasses, single-crystal alumina and magnesia depends on the environment in which they are measured. For example, the hardness of SiO_2 measured in air is lower than that measured in toluene. In addition, the hardness values measured in air are found to decrease with increasing loading time, while those measured in toluene are found to be independent of loading time [12]. Westbrook [19, 20, 24] attributed the time-dependent hardness in air to the absorption of water on the specimen surface, and later Tomazawa and Hirao [13] presented evidence from infrared absorption spectra that this diffusion of water is the cause of the observed decrease in hardness with increasing loading time. In SiO_2, it is also shown that the crack initiation load depends on the liquid in which it is measured and decreases with loading time in water [25]. But studies on the mechanism of indentation-induced crack initiation and propagation have been carried out almost exclusively on glasses [17–25].

Recently the fundamental deformation processes in single crystal Al_2O_3 have been identified as being due to basal twinning and pyramidal slip [16]. Incipient microcracks are observed at both the twin interfaces and the slip planes, and both act as nucleation sites for the ensuing radial and lateral cracks. As Al_2O_3 has applications in the biomedical field (in the form of artificial bones) and has to stay in an ambient environment for a long time (10–20 years) it is interesting to know the long-time contact-induced crack propagation in different liquids, particularly in bio-simulating liquids. In the present work, long-time Vickers' microhardness and crack-length measurements in bio-simulating, aqueous and non-aqueous liquid environments on Al_2O_3 are analysed, in order to discover the role of the liquids on crack propagation. The possible interaction between the structure of α-Al_2O_3 and the liquids during crack propagation is discussed.

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2. Experimental Procedure

Surfaces of sintered polycrystalline slabs of α-Al_2O_3 (1 cm diameter, 1 mm thickness) were prepared by NGK, Brazil. The slabs were mechanically polished using different grades of carborundum powder, and finally diamond paste. The surfaces were then etched in hydrofluoric acid and subsequently rinsed in acetone to remove fine particles.

As a simplified model for abrasive wear and erosion of ceramics, the fracture characteristics of the surface were investigated by introducing surface cracks. The Vickers' indentation method was used to produce cracks using a Rockwell Diamond tester, type BDL 3B. The indentations were performed in both air and chemical environments at room temperature (25 °C). Different loads (10–60 kg) for different indentation times (5–24 h) were used in order to see the crack variation. The chemical environment was created by placing few drops of chemical on the surface before indentation. To ensure the environment, refilling was carried out during the long-time indentations. After indentation, the liquid was wiped off with a soft paper absorber and was naturally dried at room temperature. At least six indentations were made at each load and time, and the average effect of all of them was considered.

The residual indentation impression and radial cracks were observed under the optical microscope, Neophot 21 (Carl Zeiss, Jena). Surface penetration around the indentation was observed with interference patterns using an interference attachment. A monochromatic light source of $\lambda = 589.3$ nm was used for interference.

The indentation impression and radial cracks were also observed with the help of a luminescent liquid which is produced specially for crack revelation. This solution, when spread on the surface of the indented region, penetrates in to the microcracks and produces visible luminescence under ultraviolet radiation. Hereafter the liquid is referred to as crack-revealing luminescent liquid (CRL liquid). (CRL liquid, supplied by NGK of Brazil, is an organic liquid, exact composition not published.) A convergent lens before a Philips UV lamp (RVM 125 W) was also used to improve the intensity of light on the surface of the sample. The diagonal length of the impression and crack lengths were measured both directly under the microscope, and with the help of CRL liquid, with an accuracy of 0.5 μm. Most times the lengths of the radial cracks were found to be unequal; thus an average was taken for each indentation. The chemical environments used were CRL liquid; humid air (nearly 20% water); silicon oil; ring solution (a biochemical liquid useful in simulating the biomolecules around the bones of human body: 0.60 g NaCl, 0.03 g KCl, 0.22 g dehydrated $CaCl_2$, 0.31 g sodium lactate in 100 ml water); water; pentanol; and acetonitrile. In the broad sense, the environments used were classified as (i) non-aqueous (CRL liquid); (ii) aqueous (H_2O, Ring solution, humid air); and (iii) organic (pentanol, acetonitrile).

3. Results and discussion

Fig. 1 represents optical micrographs of the indentation mark and radial cracks observed (a) directly and (b) with CRL liquid under the microscope. The indentation was made on the surface of α-Al_2O_3 in the presence of water by a Vickers' indentor loaded with 30 kg for 24 h. From Fig. 1, it can be noticed that all the radial crack lengths emanating from the tips of the impression left by the diamond indenter are not equal. Fig. 2 represents an interference pattern surrounding the impression observed under monochromatic radiation. This reveals that the surface around the impression is pressed, indicating a change in the surface energy.

Fig. 3 represents the variation of average radial crack length (ARCL) measured on the surface of α-Al_2O_3 in the presence of water, CRL liquid and pentanol, with time. The cracks are produced by applying 30 kg load on the Vickers' indentor. It can be seen from Fig. 3 that the ARCL depends on the environment in which it is measured, and increases a little faster at the beginning and later slows down. Among the three different environments, H_2O shows this behaviour clearly; until 30–40 s the increase is rapid and thereafter slows down. Also, ARCL is highest in the presence of pentanol and lowest in CRL

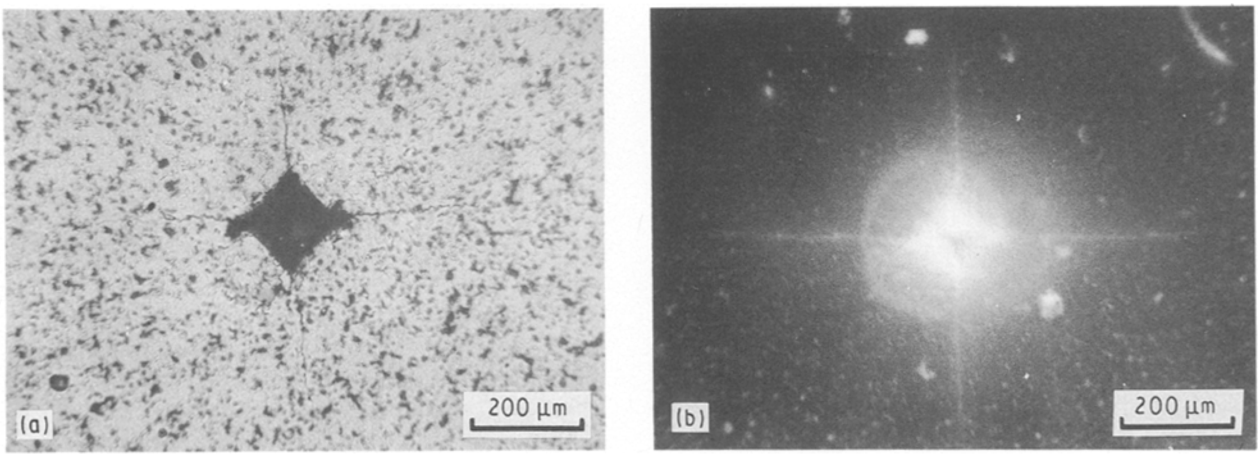

Figure 1 Optical micrographs of the indented surfaces of α-Al_2O_3 in water, showing the indentation mark and radial cracks observed directly (a) and by applying CRL liquid (b) under the microscope. The indentation was made for 24 h with 30 kg of load on a Vickers' indentor.

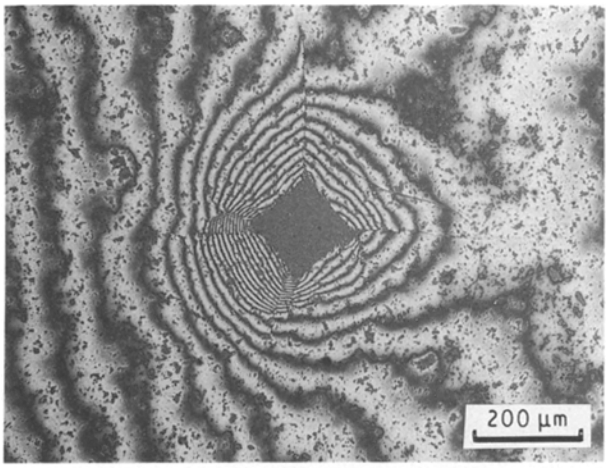

Figure 2 Optical micrograph of an interference pattern surrounding the indentation impression on the surface of α-Al_2O_3 under a monochromatic radiation of $\lambda = 589.3$ nm. The variation in the fringe width around the impression indicates that the surface depth is not uniform along the radial direction.

liquid. It is a well-established fact that the surface energy changes in the presence of solvent [25]. As different chemical environments have different abilities to change the surface energy, the crack lengths are different in different environments. With time, the ARCL depends on the reactability of the molecule of a chemical with the host molecule at the crack tip. The fact that the rate of ARCL corresponding to pentanol is more than that of water may be due to the inner crack defects produced under stress and in the presence of molecules of reactive nature (pentanol), which in turn may reflect on the crack length. The low ARCL in CRL liquid may be because of its non-aqueous nature.

The variation of ARCL with an increase in load, applied for 15 min in humid air and in different chemical environments, is shown in Fig. 4. A similar variation corresponding to ring solution is shown in Fig. 5. It can be seen from Fig. 4 that (i) the ARCL at a given load increases in different environments in the following order: CRL liquid < humid air < silicon oil < ring solution < H_2O < pentanol < acetonitrile; (ii) in air and other liquids, the crack length increases linearly with the increase in load; (iii) at every load ARCL is lowest in CRL liquid and highest in acetonitrile; and (iv) all the lines have a negative intercept on the y axis.

All the above observations can be explained, as for SiO_2, by a process called dissociative chemisorption [13, 15]. Chemicals, such as water, that lower the surface energy of a solid will ultimately reduce the strength of the material and cause the crack tip to propagate slowly by sequential rupturing of interatomic bonds. It was shown that the amount of energy required in SiO_2 to rupture the silicon–oxygen bond between two silicate tetrahedra drops by a factor of nearly 20 in the presence of water. In brief, the chemical reaction between the silica and the water reduces the amount of energy that must be supplied to make the crack extend. The model of dissociative chemisorption for crack-tip bond rupture predicts that the chemicals must be able to donate electrons to the formation of a bond with one of the host atoms (other than oxygen) at the crack tip, and also to donate a positively charged hydrogen atom to bind with the oxygen atom that was once attached to the host atom.

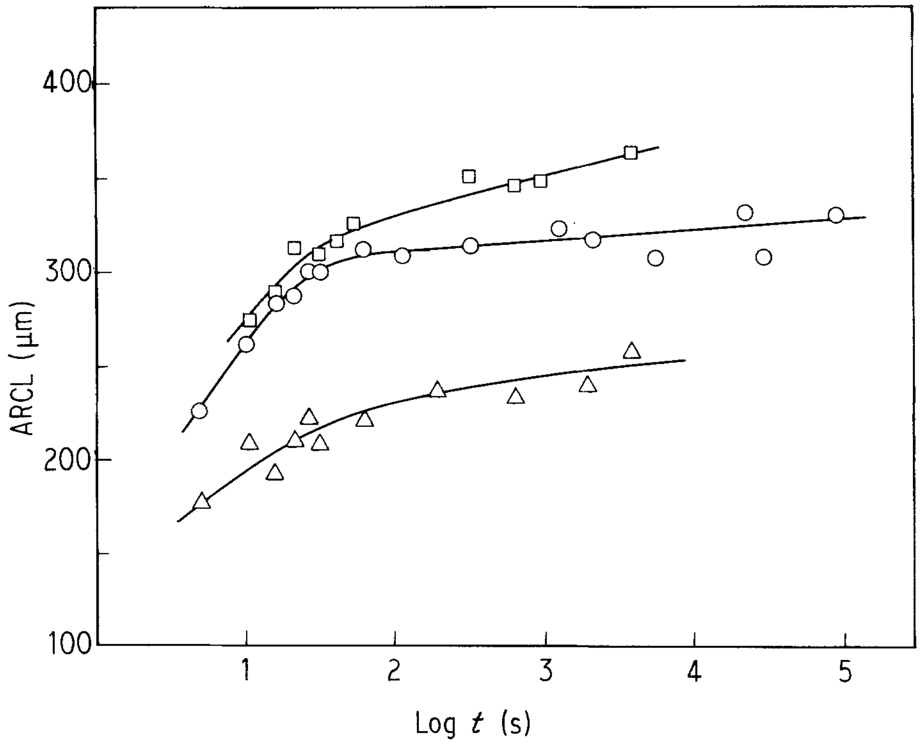

Figure 3 Variation of ARCL with time in three different liquid environments: ○, H_2O; △, CRL liquid; □, pentanol. The cracks are produced on surfaces of α-Al_2O_3 at 30 kg of load. Fast and slow regions of increase in ARCL with time in all the liquids are noticed.

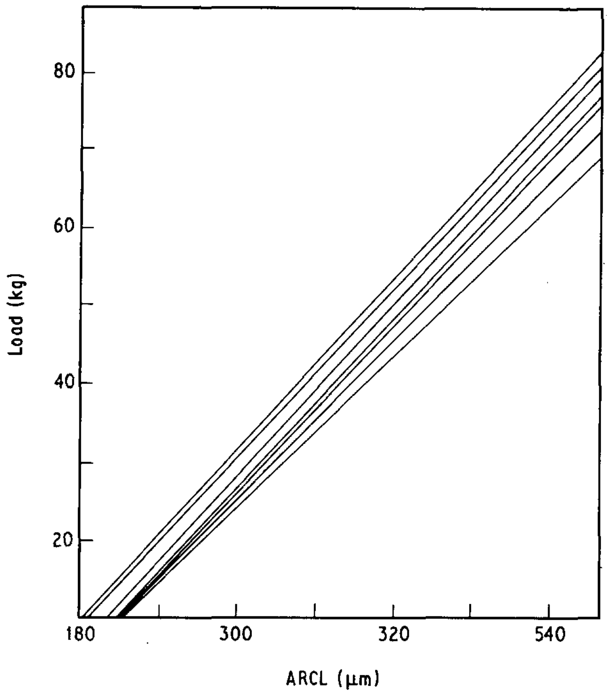

Figure 4 Variation of ARCL with load showing similar straight line behaviour in the presence of different environments. Least-square fits are made on a computer to draw the straight lines. For clarity, the experimental points are omitted. The lines (from the top down) correspond to CRL liquid, humid air, silicon oil, ring solution and water, and are almost parallel; the last two straight lines, corresponding to pentanol and acetonitrile, are neither parallel to a line corresponding to that of water, nor to one another.

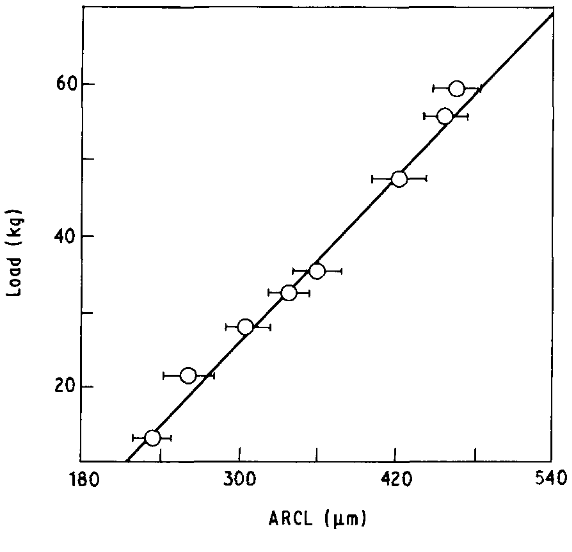

Figure 5 Variation of ARCL with load in the presence of ring solution. Each load applied for 15 min. Experimental points with error bars are shown; straight line drawn after the least-square fit on a computer.

In addition, a single molecule of the chemical must be small enough to fit into the crack tip in such a way that breaking and forming of the bonds can take place simultaneously.

The rate of crack growth depends not only on the chemical environment, but also on the magnitude of the applied stress. In the absence of stress the surface of the ceramic reacts very slowly with water. The surfaces are so unreactive toward water that they will not even absorb water vapour. Yet the application of stress on SiO_2 surface can cause cracks to grow at speeds greater than 1 mm s^{-1}, whereas its surface dissolution rate without stress is about 10^{-17} m s^{-1} [15]. The crack tip focuses stress, the higher the stress becomes, until it reaches several million N m^{-2} within a few atomic dimensions of the tip. Exposed to these large stresses, the atomic structure of the ceramic becomes distorted from its normal bonding configuration. Theoretical calculations show that if a silicate tetrahedron is distorted by pulling on the corner oxygen atoms, the silicon atom in the centre is more likely to bond with a water molecule. Furthermore, the chemical interaction with water will decrease the force required to distort the metal–oxygen bonds. A similar mechanism of dissociative chemisorption under stress is possible in Al_2O_3, as there are six oxygen atoms surrounding the aluminium.

Fig. 4 also shows that the crack length in Al_2O_3 increases with the increase in water content (humid air to pure water). These observations are strongly dependent on both the load and the environmental conditions employed for indentation. Hirao & Tomazawa [25] have also observed in SiO_2 that the diagonal of the knoop indentation depends on stress and chemical environment. Under these experimental conditions, the change in hardness was attributed by them to the change in surface energy. Our results on Al_2O_3 in aqueous environments are therefore probably due to the reduction of surface energy modified under stress, and the action of the molecules of water at the crack tip. In the presence of pentanol and acetonitrile, liquids of big molecular size, the crack lengths are greater than those in aqueous liquids. The reason may be due to (i) their nature of accepting water from air, although they do not originally contain water, or (ii) their reactive nature with Al_2O_3. However, in all the liquids the ARCL has a similar variation (linear) with load. This similarity leads us to examine each variation in detail, in order to discover the possible common reasons. Thus in the following discussion the observed crack-length behaviour will be sought.

Considering the contribution of the surface energy to hardness, originally suggested by Bernhardt [26], Frohlich *et al.* [27] and later by Hirao & Tomozawa [25], the average diagonal length of the Vickers' indentor impression, h, and the applied load, L, are related as

$$L = a_1 h + a_2 h^2 \qquad (1)$$

where a_1 and a_2 are constants. As the radial crack propagation is one dimensional and the experimental variation of crack length, l, with applied load is linear in each liquid environment, we write the relation between L and l as

$$L = A_1 + A_2 l \qquad (2)$$

where A_1 and A_2 are new positive constants. The values of the coefficients A_1, corresponding to the intercept, and A_2, corresponding to the slope of the line, are obtained for all the curves of Fig. 4 and are also given in Table I. It can be seen from this table that the value of A_1 is negative for all the curves and A_2 is

TABLE I The constants A_1 and A_2, obtained by fitting the crack-length data of Fig. 4 with Equation 2, and the percentage increase in crack length with respect to CRL liquid corresponding to different environments.

Medium	A_1 (kg)	A_2 (kg μm^{-1})	Percentage increase in crack length
CRL liquid	22.94	0.1816	–
Humid air	24.10	0.1818	2.719
Silicon oil	26.19	0.1811	9.349
Ring solution	28.91	0.1816	14.682
Water	28.16	0.1831	16.147
Pentanol	25.64	0.1698	–
Acetonitrile	23.93	0.1608	–

almost constant, except for those corresponding to acetonitrile and pentanol: the values of A_2 corresponding to the environment of acetonitrile and pentanol are slightly lower than the rest.

The first constant on the right-hand side of Equation 2 represents the energy reduction due to chemisorption towards the propagation of linear cracks, while the other constant represents the surface energy contribution. This can be seen by integrating both sides of Equation 2 with respect to l from 0 to l. Then the left-hand side of the equation, $\int L dl$, corresponds to the total work performed during the indentation and the first term of the right-hand side after integration, $A_1 l$, to the energy reduction to create a crack of length l (as A_1 is negative). The second term on the right-hand side after integration, $A_2 l^2/2$, corresponds to the work needed to create the new surface. Therefore A_1 and A_2 indicate a qualitative measure of the energy reduction needed to produce a crack, and the energy needed to create a new surface, respectively. From Table I, it can be seen that the constant A_1 increases (absolute value) with the increase in concentration of H_2O and reaches a maximum in water. The other constant, A_2, is almost the same, corresponding to all the aqueous liquids. These variations indicate that H_2O reacts with Al_2O_3 at the crack tip to form aluminium hydroxide and thus helps in the energy reduction needed to propagate the crack tip. Silicon oil also follows the same sequence in the sense that its corresponding coefficient A_1 is in between humid air and water, and A_2 is almost the same as that of water, indicating a negligible frictional effect and a similar reaction of the silicon atoms of the oil with the oxygen atoms of Al_2O_3, to that of water molecules with the molecules of Al_2O_3. The constants A_1 and A_2 corresponding to acetonitrile and pentanol are slightly less than those corresponding to water and other environments. The reason for low values of A_1 could be the larger molecular sizes of acetonitrile and pentanol than of Al_2O_3. As these large molecules cannot reach the exact tip of the crack, their action at the tip could be assumed to be less. A similar observation in SiO_2, using liquids of large molecular size such as toluene, was made by Michalske [15]. The lower values of A_2 may be attributed to the following special characters of these liquids. Pentanol, being highly reactive towards aluminium, forms aluminium hydroxide and thereby reduces the surface energy. Acetonitrile, although, non-reactive with Al_2O_3, is very hygroscopic in nature, and thus always absorbs water molecules from the air medium and causes water to react with the surface of alumina. But the higher crack lengths than in pure water could be due to a special type of reaction of the cyanide group with Al_2O_3 under high stress. However this needs further investigation.

To strengthen the observation of the same surface energy in the presence of cracks and of environments consisting of water, we have studied the variation of hardness with time. The observations are shown in Fig. 6. From this figure we find that the hardness, in the presence of all the aqueous liquids, decreases by the same straight line with an increase in time. The time variation of the crack length (Fig. 3) and the way the hardness decreases (both in presence of liquids) indicate that the energy supplied by the load on the indentor is used mostly in increasing the length of the crack, and is also governed by the chemisorption at the tip of the crack.

Since the chemical reactions at the crack tip are very slow, long-time crack propagation can be assumed to reveal an apparent difference in crack length. Therefore, cracks were produced on an Al_2O_3 surface by applying 30 kg of load on the indenter for a duration of 24 h in the presence of different environments. The measured values of ARCL thus produced are given in Table I. It is seen from the table that the CRL liquid has the minimum crack length. The percentage rise in crack length in presence of other liquids, when compared to CRL liquid, are also given in Table I. It may be noted that the percentage rises in crack length under ring solution and water are almost the same: this may be due to the high percentage of water in ring solution. Determination of the long-time percentage rise in the presence of acetonitrile and pentanol is not possible as the liquids are volatile. The reason for the minimum crack length in CRL liquid may be the blunting of water molecules by the CRL liquid molecules at the site of the crack tip. This is confirmed by observing the long-time crack lengths in the presence of CRL liquid, added with different percentages of H_2O. These results are shown in Fig. 7. It can be seen

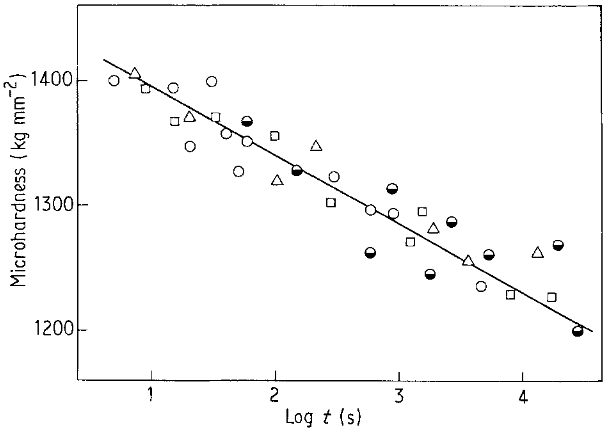

Figure 6 Variation of microhardness with time in different environments. A load of 30 kg is applied for 10 s on the surface of α-Al_2O_3. Hardness in each environment follows the same linear variation with increase in time. (○) water, (△) humid air, (□) CRL liquid, (◒) ring solution.

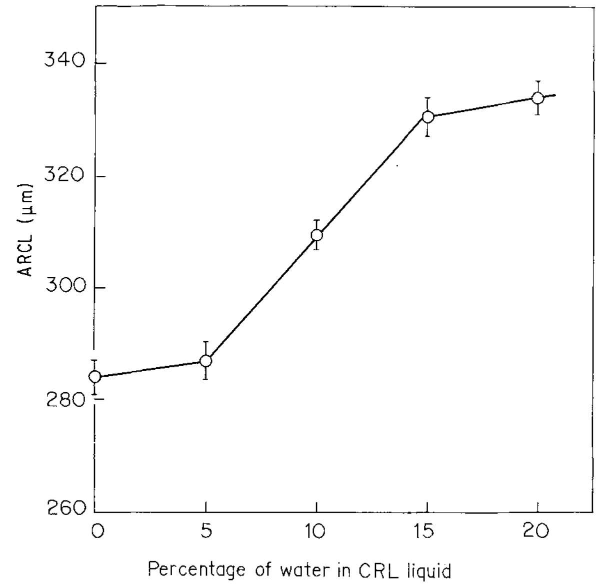

Figure 7 Variation of ARCL in the presence of CRL liquid mixed with different percentages of water. The cracks are produced at 30 kg load applied for 24 h. As the water percentage becomes equal to 20, the ARCL becomes equal to that in the environment of pure water.

from this figure that the ARCL increases slowly until the water percentage in CRL liquid reaches 5, then rapidly to 15, and later approaches a value almost equal to the ARCL in pure water, when the percentage becomes equal to 20. Hence it may be concluded that the water reactibility at the crack tip on an Al_2O_3 surface under stress is greater, and therefore the bioliquids and artificial structures of Al_2O_3 will be useful, considering the effect of water molecules, to give long durability to artificial bones and other prostheses made of Al_2O_3 or other, similar ceramic materials.

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References

1. B. R. LAWN and T. R. WILSHAW, *J. Mater. Sci.* **10** (1975) 1049.
2. B. R. LAWN, in "Fracture Mechanics of Ceramics", Vol. 5, edited by R. C. Bradt, D. P. H. Hasselman and F. F. Lange (Plenum, New York, 1983) p. 1.
3. B. R. LAWN, in "Strength of Glass", edited by C. R. Kurkjian (Plenum, New York, 1985) p. 67.
4. A. G. EVANS and E. A. CHARLES, *J. Amer. Ceram. Soc.* **59** (1976) 371.
5. G. R. ANSTIS, P.CHANTIKUL, D. B. MARSHALL and B. R. LAWN, *ibid.* **64** (1981) 533.
6. P. CHANTIKUL, G. R. ANSTIS, B. R. LAWN and D. B. MARSHALL, *ibid.* **64** (1981) 539.
7. J. T. HAGAN and M. V. SWAIN, *J. Phys. D.* **11** (1978) 2091.
8. J. T. HAGAN, *J. Mater. Sci.* **15** (1980) 1417.
9. B. R. LAWN, T. P. DABBS and C. J. FAIRBANKS, *ibid.* **18** (1983) 2785.
10. D. B. MARSHALL and B. R. LAWN, *ibid.* **14** (1979) 2001.
11. D. B. MARSHALL, B. R. LAWN and P. CHANTIKUL, *ibid.* **14** (1979) 2225.
12. K. HIRAO and M. TOMOZAWA, *J. Amer. Ceram. Soc.* **70** (1987) 377.
13. M. TOMOZAWA and K. HIRAO, *J. Mater. Sci.* **6** (1987) 867.
14. T. A. MICHALSKE and B. C. BUNKER, *J. Amer. Ceram. Soc.* **68** (1985) 586.
15. *Idem, J. Appl. Phys.* **56** (1984) 2686.
16. H. M. CHAN and B. R. LAWN *J. Amer. Ceram. Soc.* **71** (1988) 29.
17. K. YAMANAKA and Y. ENOMOTO, *J. Appl. Phys.* **53** (1982) 846.
18. M. MUNAWAR CHAUDHRI, *Phil. Mag.* **53** (1986) L55.
19. J. H. WESTBROOK and P. J. JORGENSON, *Trans. AIME* **223** (1965) 425.
20. J. H. WESTBROOK and P. J. JORGENSON, *Amer. Mineral.* **53** (1968) 1899.
21. J. F. KRANICH and SCHOLZE, *Glastech. Ber.* **49** (1976) 135.
22. S. P. GUNASEKERA and D. G. HOLLOWAY, *Phys. Chem. Glasses.* **14** (1973) 45.
23. C. J. FAIRBANKS, R. S. POLVANI, S. W. WIEDERHORN, B. J. HOCKEY and B. R. LAWN, *J. Mater. Sci. Lett.* **1** (1982) 391.
24. J. H. WESTBROOK, in "Environment-Sensitive Mechanical Behaviour", edited by A. R. C. Westwood and N. S. Stoloff (Gordon & Breach, New York, 1966) p. 247.
25. K. HIRAO and M. TOMOZAWA, *J. Amer. Ceram. Soc.* **70** (1987) 497.
26. E. O. BERNHARDT, *Z. Metallkde* **33** (1941) 135.
27. F. FROHLICH, P. GRAU and W. GRELLMANN, *Phys. Status Solidi* **42** (1977) 79.

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