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# Influence of Environment on Delayed Failure of Alumina Ceramics

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## Abstract

*Subcritical crack growth in alumina ceramics is a phenomenon that arouses interest with respect to the problems of performance of various engineering parts, e.g. seal rings, bearings, etc. The subcritical crack growth results in dependence of strength on time known as delayed failure. Effect of environment on subcritical crack-growth exponent for various alumina-base ceramics is studied. A dynamic fatigue technique is utilized. It is revealed that the subcritical crack-growth resistance of glass-bonded aluminas is significantly lower than that of high-purity alumina in air and in water. Only negligible difference was revealed in the delayed failure behaviour of ceramics bonded with various common glassy phases. However, high-purity alumina ceramics are much more susceptible to fatiguing in an acidic environment compared to the yttria-alumosilicate glass-bonded alumina: hydrochloric acid environment reduces drastically the crack-growth velocity exponent due to the low stress–corrosion resistance of magnesia-enriched interfaces in high-alumina ceramics. © 1998 Elsevier Science Limited. All rights reserved*

## 1 Introduction

Alumina ceramics are good candidates for applications involving corrosion-active media, e.g. in seal-rings, bearings and impellers in pumps. However, as for many oxide ceramics, their strength is susceptible to deterioration in chemical environments.[1–5] This phenomenon is believed to result primarily from a stress-enhanced chemical reaction between the environment and the bonds at the tips of microstructural stress concentrators, such as microcracks, pores and grain boundaries.[1,6–9] As a consequence of these reactions, alumina ceramics exhibit subcritical crack growth prior to catastrophic failure, and their strength and fracture are dependent on time or stressing rate.

Generally, it is considered that there are three regions of the kinetic crack growth law in ceramics.[1] The first of these, region I, is where the crack growth is thought to be reaction-rate limited and is a major contributor to the ceramics lifetime. This region is empirically described by the relation between crack-growth velocity, $v$, and the applied stress intensity factor, $K$, as follows

$$v = AK^n \tag{1}$$

where $A$ is a constant and $n$ is the crack velocity exponent. These controlling parameters of crack growth are thought to be both material and environment dependent.[1,7–11] Preliminary investigations suggest that glassy grain-boundary phases in aluminas significantly increases the material's sensitivity to subcritical crack growth, making such ceramics less resistant to fatiguing than those without glassy phase.[12] The principal component of glassy phase, silica, causes separation and cracking by hydration reaction which include the interaction of incoming water molecule with the stretched Si–O–Si crack-tip bond and the formation of Si–OH.[4] A model of this interaction has been devised in Ref. 6. The pH value at the crack tip seems to be the main factor in this phenomenon influencing the changes in strength. In particular, it has been revealed for silica-base glasses that the slope of the crack velocity versus stress intensity factor plot in low pH aqueous solutions (acidic region) is about twice that in high pH solutions

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(basic region).[10] Similar slope variations were obtained from dynamic fatigue studies of various glasses in water.[11] The glasses containing highly basic constituents such as alkali ions were shown to exhibit slopes that were less by a factor of 2 than glasses such as silica that contained no basic constituents. The components of the glass reacting with environment controls the pH value of the solution at the crack tip influencing the crack-growth velocity exponent. The mutual effects on crack velocity exponent of both the composition of testing media and the dissolution of tested material are supposed to be much complicated. For example, it was shown that the mean crack velocity in soda-lime silicate glass reaches a maximum at a certain pH value of the testing media, of about 10·5.[13] The mean crack-growth velocity was estimated to be higher in neutral than in acidic region, being approximately invariable in the pH range of 1 to 4.[13]

In the alumina ceramics processing, sintering additives are often utilized which form the grain-boundary phase. The behaviour of such a phase may control the subcritical crack growth process. In this context, the present study is aimed at investigation of the influence of environment on subcritical crack-growth exponent for aluminas sintered with various additives. The results of this study can be used in designing with the alumina ceramic parts for certain applications in corrosive aqueous media.

## 2 Experimental Procedure

Experiments were performed with the specimens of four series of alumina ceramics prepared by cold uniaxial pressing followed by sintering. The ceramics were:

A1: 99·5 wt% alumina with sintering additive of 0·4 wt% MgO, the total impurities content (silica, alkali oxides) is no more than 0·1 wt%;

A2: 95 wt% alumina bonded with glassy grain-boundary phase in the system $Y_2O_3$–$Al_2O_3$–$SiO_2$, the composition of the sintering additive is (in mol%): $Y_2O_3$ 8, $Al_2O_3$ 15, $SiO_2$ 77;

A3: 95 wt% alumina bonded with glassy phase in the system $Me'_2O$–$Me''O$–$B_2O_3$–$SiO_2$, where $Me'$ is Na and K, $Me'$ is Mg, Ca and Ba, the composition of the sintering additive is (in mol%) $Me''O$ 30, $B_2O_3$ 30, $SiO_2$ 25, $Al_2O_3$ 14,5, $Me_2O$ 0·5;

A4: a commercial glass-bonded alumina ceramics GB-7, its composition is as follows (in wt%): $Al_2O_3$ 97·1, $SiO_2$ 0·9, CaO 0·9, $B_2O_3$ 0·92, $Na_2O$ 0·09, impurities—up to 100%.

The features of the microstructure of ceramics are as follows:

A1: pore-free ceramics with the equiaxial alpha-alumina grains of average size about 11 $\mu$m;

A2: pore-free material with the elongated grains having the size in the range of 5–35 $\mu$m, the glassy phase occupies about 13 vol%;

A3: pore-free materials containing about 12 vol% of the grain-boundary glassy phase. There are elongated alumina grains of about 15–40 mm length and 7–15 $\mu$m thickness. These grains are surrounded by glassy-phase layers, the latter being about 2 $\mu$m thickness.

A4: ceramics with content 91–92 wt% of crystalline and 8–9 wt% of glassy phase; the alumina grains are up to 15 $\mu$m length.

To evaluate the crack velocity exponent, $n$, a dynamic fatigue test method was chosen, where strength is measured as a function of straining rate.[1,3,11,14,15] The specimens of $7\times8\times35\,\text{mm}^3$ size were loaded in a stiff corrosion-resistant three-point adjustment at a span of 32 mm. The tests were performed in ambient air atmosphere at relative humidity RH = 59–62% and a temperature 20–22°C, in water, in 0·1 N HCl solution (pH = 1), and in a mixture of 0·1 N HCl with a buffer solution which has been prepared by mixing of citric acid and NaOH (pH = 2). The sample size was 10 to 20 specimens for each test. A UTS-100 screw-drived testing machine (UTS Testsysteme GmbH, Germany) was utilized. The cross-head speed of testing machine was in the range 0·03 to 15 mm $\text{min}^{-1}$. Data from the dynamic fatigue test were least-squares fitted to the equation

$$\log\,\sigma = C + [1/(1+n)]\log\varepsilon' \tag{2}$$

where $\sigma$ is the measured strength; $\varepsilon'$ is the straining rate; $C$ is a constant.[15]

Equation (2) is derived from the relation

$$\sigma^{n+1} = 2E\varepsilon'\sigma_{Ic}^{n-2}/(n-2)AY^2K_{Ic}^{n-2} \tag{3}$$

given in Ref. 1 and can principally be applied to estimate the $n$ value in the assumption that

$$K_{Ic} = Y\sigma_{Ic}\sqrt{a_i} \tag{4}$$

where $K_{Ic}$ and $\sigma_{Ic}$ are the critical stress intensity factor and the strength in an inert environment or determined by very fast loading (negligible crack extension).[15] In eqns (3) and (4) $E$ is the modulus of elasticity and $a_i$ is the initial flaw size. Invariance of the $K$-calibrating polynomal $Y$ is assumed too. It follows from eqns (2) and (3) that the value of $n$ can be evaluated from the slope of the log $\sigma$ versus log $\varepsilon'$ plot if $K_{Ic}$ is supposed to be invariant with respect to the testing media. It was *a priori* assumed that this condition is satisfied at the cross-head speed of 15 mm $\text{min}^{-1}$ (the highest in our experiments). An extrapolation of the experimental data for the A1 series ceramics to the strength value at the straining rate of $10^{-2}\,\text{s}^{-1}$ in air, water and acids results in log $\sigma$ values in the range of 2·37–2·38. Therefore, the strength (and the critical stress intensity factor) is approximately nonvariable with respect to the testing media at the cross-head speed of 15 mm $\text{min}^{-1}$, in accordance with the above assumption.

Fracture toughness $K_{Ic}$ was measured by three-point bending of single-edge notched beam (SENB) specimens. A thin notch of 0·5 specimen's width was machined with a diamond saw-wheel. The measured curvature radius of the notch tip was ca. 50 $\mu$m. The specimens were loaded at a span of 32 mm. To calculate $K_{Ic}$, a common polynomal $Y$ for wide range stress intensity factor was utilized.[16]

## 3 Results and Discussion

The strength was dependent on the composition of the specimens, probably due to the differences in the grain size and microstructural features.

Figure 1 shows the dynamic fatigue data for the specimens tested in air. The strength increases generally with an increase in straining rate. A fit of the experimental data to eqn (2) results in the $n$-values given in Table 1.

The crack velocity exponent for all the glass-bonded aluminas is lower than that for 99·5% alumina ceramics when tested in air, being approximately invariable for all the glass-bonded materials. Somewhat more fatigue resistant are the specimens of A2 series as compared to the specimens of A3 and A4 series.

Figure 2 shows the strength versus straining rate plots for A1, A2 and A3 series tested in water. The results of evaluation of the crack velocity exponent are given in Table 1. The water content in environment decreases slightly the crack velocity exponent for the specimens of the A1 and A2 series. These data are in accordance with known estimations of $n$ value in the range 35 to 68 for aluminas in an aqueous environment.[14]

Shown in Figs 3 and 4 are the dynamic failure plots for A1 and A2 series tested in acidic solutions with pH = 1 and pH = 2, respectively. A fit of these data to eqn (2) results in $n$ values given in Table 2. By comparison of the $n$ values for these ceramics tested in humid air and in water, it can be concluded that hydrochloric acid reduces drastically the resistance of the 99·5% alumina–0·4% magnesia

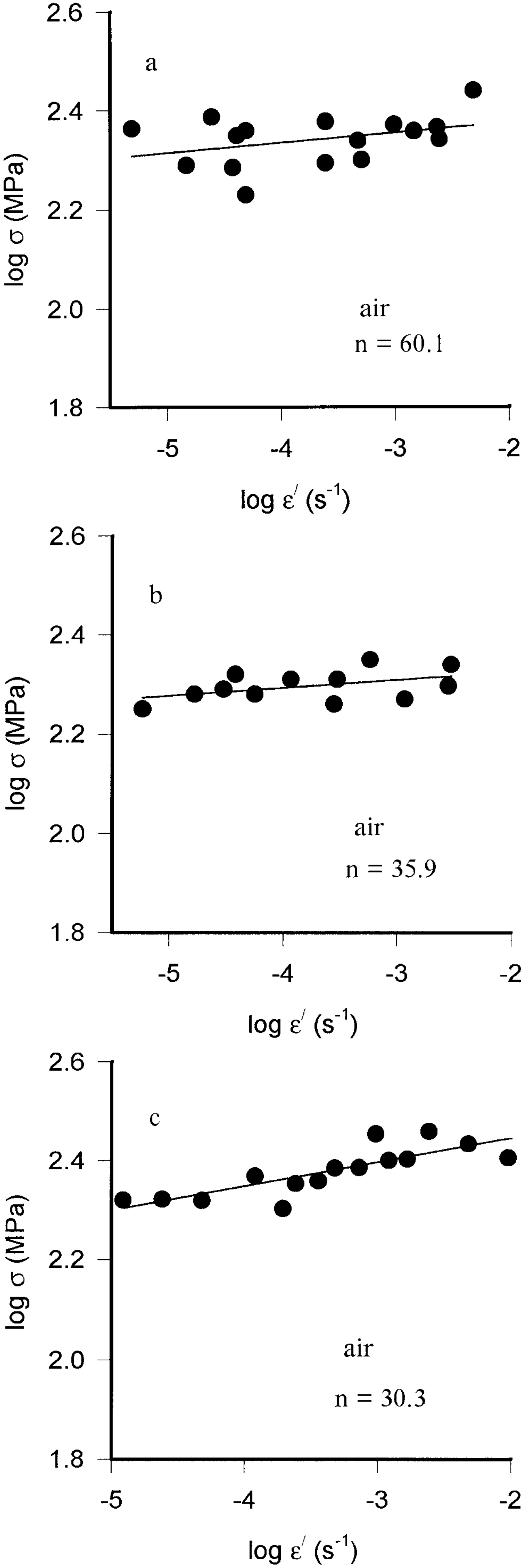

**Fig. 1.** Strength versus straining rate for ceramics tested in air: series (a) A1, (b) A2 and (c) A4.

**Table 1.** Crack velocity exponent for the specimens tested in air and in water

| *Series* | *Crack velocity exponent (n)* | | *Correlation coefficient (r)* | |
|---|---|---|---|---|
| | *In air* | *In water* | *In air* | *In water* |
| A1 | 60·1 | 54·2 | 0·50 | 0·62 |
| A2 | 35·9 | 34·8 | 0·61 | 0·47 |
| A3 | 32·3 | 32·8 | 0·42 | 0·58 |
| A4 | 30·3 | | 0·82 | |

ceramics to delayed failure while does not practically affect the crack-velocity exponent for the glass-bonded ceramics of A2 series. So, the difference in behaviour of these ceramics is obvious, as it can be seen in Fig. 5 summarizing these data.

Scanning electron microscopy revealed that the mode of crack propagation changes from mixed trans- and intergranular in air to the predominant intergranular when the specimens were tested in acid. It can particularly be seen in Fig. 6 where the micrographs of the fracture surface of A1 ceramics tested in air, water and acidic solution with pH = 1 are shown. Therefore, the behaviour of grain boundaries with respect to environment seems to be the major factor influencing the subcritical crack propagation. This behaviour influences the critical stress intensity factor too. In particular, the fracture toughness $K_{Ic}$ of the A1 ceramics as measured at a moderate cross-head speed of 0·2 mm min$^{-1}$ decreases from 3·8 MPa m$^{1/2}$ for the specimens tested in air to 3·4 MPa m$^{1/2}$ for these tested in water, and further to 2·9 MPa m$^{1/2}$ when the test was performed in acidic media at pH = 1. Measured in acidic environment, the critical stress intensity factor depends strongly on straining rate (Fig. 7). A least-squares fit of these data to the linear-regression equation

$\log K_{Ic} = A + m \ \log \delta'$, where $\delta'$ is the straining rate (testing machine cross-head speed) gives $m = 0{\cdot}083$ and $A = 0{\cdot}576$. Therefore, the slow crack growth is assumed to occur during the fracture toughness test of the SENB specimens.

Assuming the subcritical crack growth in ceramics is reaction-rate limited, it becomes clear why the water content in environment (tests in humid air and in water) has only a small effect on the crack velocity exponent: the chemical potential of the water does not depend on state of stress at the crack tip.[8]

The principal component of the glassy grain-boundary phases in A2 and A4 ceramics is silica which interact actively with water under the applied stress resulting in stress-corrosion cracking.[1] Partial substitution of boron oxide for silica in the A3 ceramics does not result in decrease of the susceptibility to stress-corrosion cracking, probably because the boron oxide is highly acidic

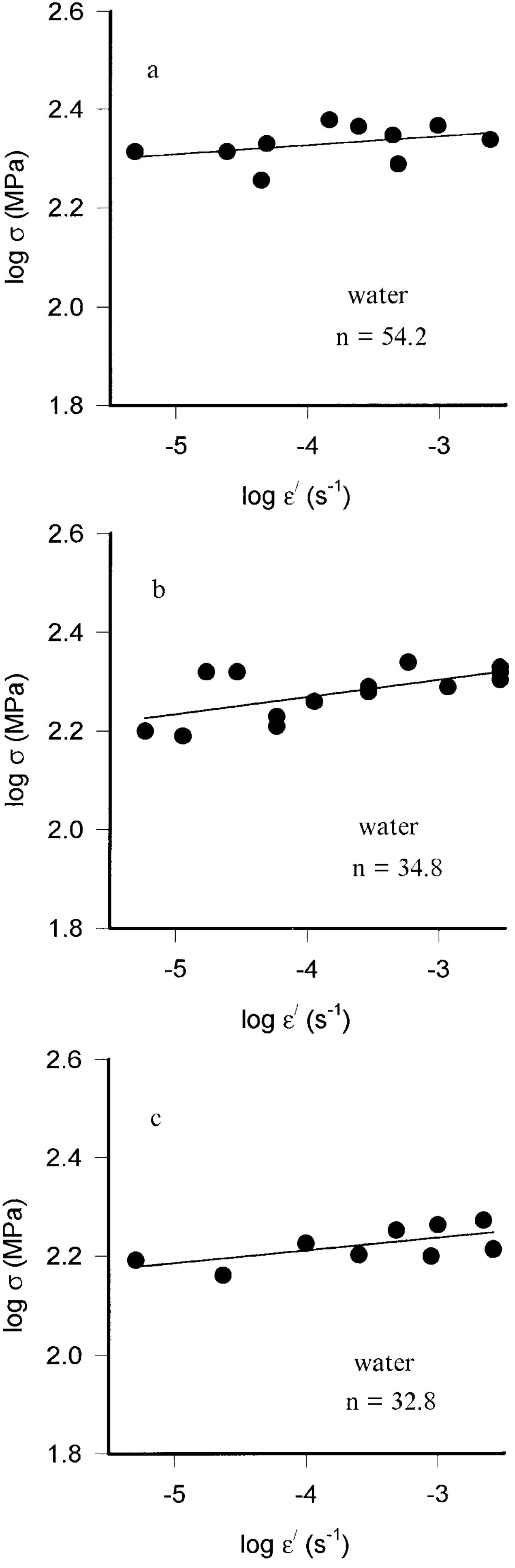

**Fig. 2.** Strength versus straining rate for ceramics tested in water: series (a) A1, (b) A2 and (c) A3.

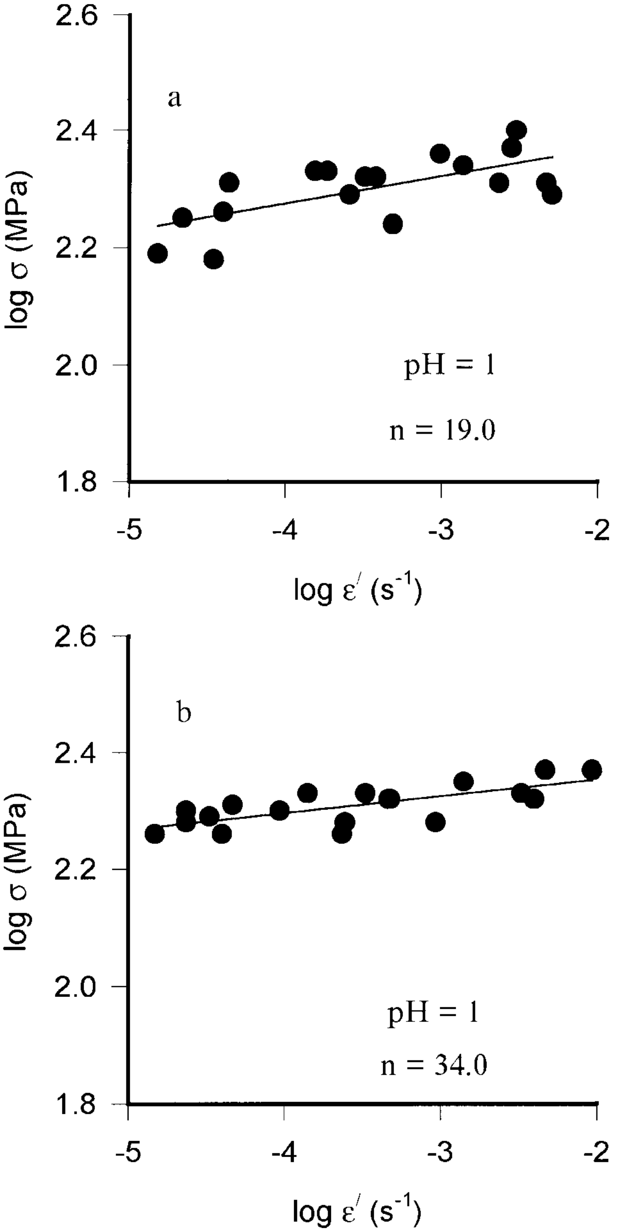

**Fig. 3.** Strength versus straining rate for ceramics tested in the solution with pH 1: series (a) A1 and (b) A2.

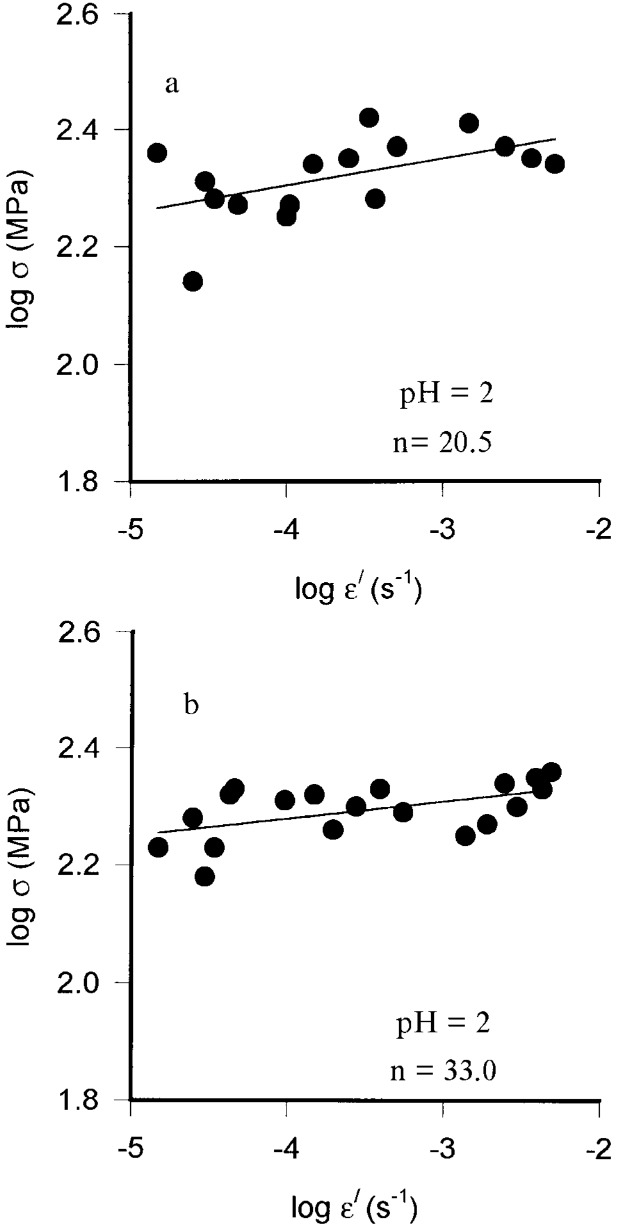

**Fig. 4.** Strength versus straining rate for ceramics tested in the solution with pH 2: series (a) A1 and (b) A2.

oxide too. The stress-enhanced dissolution of glassy phase in A2 ceramics does not promoted by acidic testing media as compared with the neutral environment (water). This is supposed to be the reason why the crack velocity exponent for A2 ceramics is approximately invariable when tested in water and in acids. This conclusion is in agreement with the experimental data indicating that the crack velocity exponent for silica-base glasses does not practically depend on the pH in the range 1 to 4.[13] Besides, these results are not contrary to the data,[10] where it has been shown that acidic environment does not decrease the crack-velocity exponent in a silica-base glass.

Contrary to the glass-bonded ceramics, the delayed failure behaviour of the 99·5% alumina is rather susceptible to the acidic environment. It is well known that magnesium ions are segregating at the grain boundaries in alumina ceramics.[17] The exact form of existence of magnesia additions within the grain boundaries is not clear yet, because the amount of MgO at the boundary is small enough as to be difficult to investigate. It could be supposed that the magnesium ions are forming the ionic bonds with oxygen within the interfaces. The ionic-bond solids are highly

**Table 2.** Crack velocity exponent for the specimens of A1 and A2 series tested in acids

| *Series* | *pH = 1* | | *pH = 2* | |
|---|---|---|---|---|
| | *Crack velocity exponent (n)* | *Correlation coefficient (r)* | *Crack velocity exponent (n)* | *Correlation coefficient (r)* |
| A1 | 19·0 | 0·70 | 20·5 | 0·57 |
| A2 | 34·0 | 0·74 | 33·0 | 0·58 |

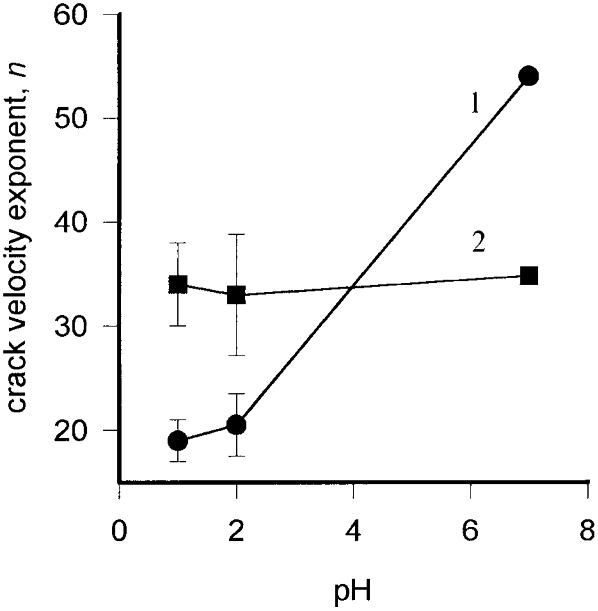

**Fig. 5.** Effect of pH on the crack velocity exponent: 1, A1; 2, A2 ceramics.

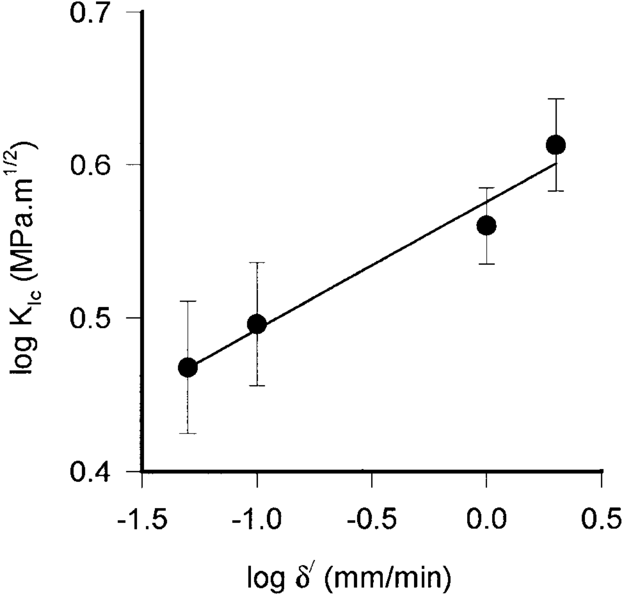

**Fig. 7.** Effect of straining rate on fracture toughness $K_{Ic}$ of A1 ceramics in acid with pH = 1.

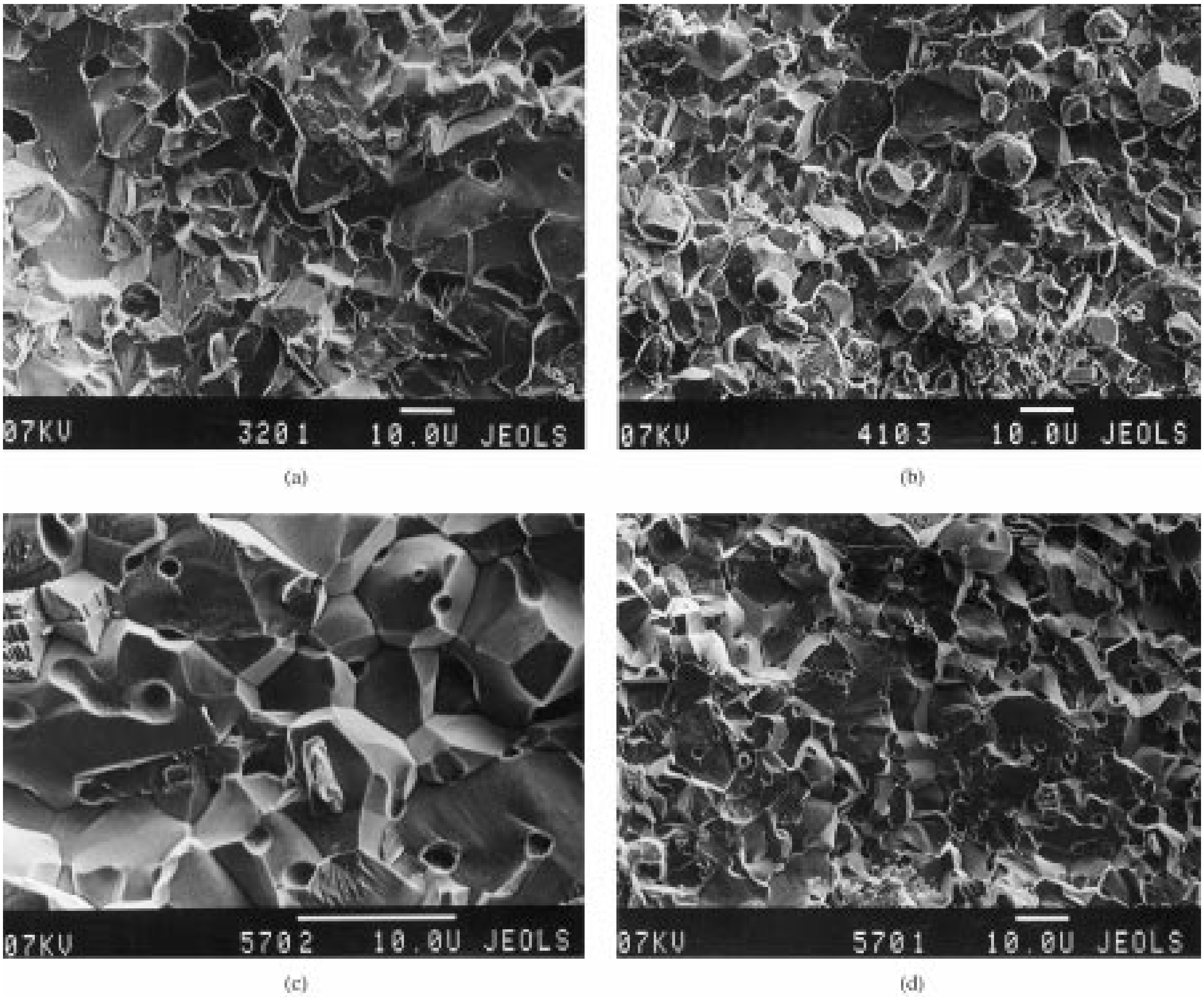

**Fig. 6.** SEM micrographs of fracture surfaces of A1 ceramics tested (a) in air, (b) in water and (c,d) in acid with pH = 1.

susceptible to stress-corrosion cracking,[7] contrary to the covalent solids like SiC or $Si_3N_4$.[1,18] For MgO of different grades this has particularly been demonstrated by delayed-failure tests in water.[19]

The crack propagation mode in 99·5% alumina–0·4% magnesia ceramics tested both in water and in acid was predominantly intergranular, while it was mixed trans- and intergranular in air. Thus, it can be assumed that the inherently low stress-corrosion resistance of the ionic Mg–O bonds at the grain boundaries is the reason for the high susceptibility of the A1 ceramics to the delayed failure in water. The acidic media enhances the chemical attack on the magnesia-containing grain boundaries resulting in a decrease of the crack velocity exponent, i.e. making the ceramics less resistant to fatiguing.

## 4 Conclusion

Dynamic fatigue tests of four alumina-base ceramics was performed in various environments. It is shown that the fatigue resistance of the glass-bonded aluminas in air is significantly less than that of the 99·5% alumina–0·4% magnesia ceramics. Crack-velocity exponent for glass-bonded ceramics is revealed to be practically invariable in respect to the composition of the glassy grain-boundary phase. Influence of the water and acidic environment on the crack velocity exponent depends strongly on the composition of ceramics. The crack velocity exponent for high-alumina ceramics decreases drastically in hydrochloric acid solutions with pH 1 and 2. This phenomenon is believed to result from the gross chemical interaction of the acid with the Mg–O bonds at the interfaces. Contrary to that behaviour, the acid environment had only slight effect on the crack-velocity exponent for the yttria–alumosilicate glass bonded ceramics. This material seems to be more reliable for the acidic-media applications than high-alumina magnesia-bonded ceramics.

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