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Effects of liquid environments on zirconia-toughened alumina

Part II *Mechanical properties*

I. THOMPSON, R. D. RAWLINGS
Department of Materials, Imperial College of Science, Technology and Medicine, Exhibition Road, London SW7 2BP, UK

The corrosion resistance of a zirconia-toughened alumina after prolonged exposure to a series of liquid environments is assessed. From the range of environments studied, only HCl caused a significant degradation in both strength and toughness. The mechanism of this deleterious behaviour was the transformation of the tetragonal zirconia particles to the monoclinic polymorph at the surface. The mechanical properties were determined by both the monoclinic content and the depth of penetration of the HCl, and hence the depth of the monoclinic-containing surface layer, with the latter probably being more important.

1. Introduction

Ceramics are generally classed as corrosion-resistant or inert materials. This is not strictly true: within the broad spectrum of ceramics there are materials that are resistant to attack by acids, alkalis, molten metals, vapours etc., but no one material will be resistant to attack by all of the above substances. In choosing a material for a given application, a ceramic composition is selected to withstand a particular environment. Modern alumina ceramics find widespread application in many industrial processes due to their chemical inertness and thermal stability. Following the findings of Garvie *et al.* [1] on monolithic zirconia, there has been considerable interest in the toughening of alumina by the incorporation of a fine dispersion of zirconia particles (called zirconia-toughened alumina; ZTA). At the present time there is little, if any, information on the corrosion resistance of ZTA. It is foreseen that ZTA could be a more suitable material than alumina in some of the more stringent service environments. The aim of the present study was to assess the resistance of ZTA to a range of industrial solutions, with the proposed application of ZTA as a material suitable for use in pump components and fluid-handling systems, a market where alumina has made considerable inroads.

It has been widely reported [2–8] that the incorporation of a dispersed second phase of stabilized zirconia particles can offer a significant increase in the strength and fracture toughness of alumina. Studies to date suggest that both stress-induced transformation and microcrack toughening contribute to this enhancement [5]. There is known to be an optimum volume fraction of ZrO_2 [9], which is in the region of 15 vol %. A more precise value cannot be quoted as it is dependent on the nature of the alumina used, the ZrO_2 particle-size distribution, the amount of stabilizing addition, and the stabilizer employed. Yttria has been the most common stabilizing agent, although recent research has investigated the role of ceria and yttria/ceria mixtures [10]. The high modulus of alumina, ~ 400 GPa, compared with ~ 200 GPa for ZrO_2, is of benefit in retaining the ZrO_2 phase in its tetragonal polymorph at room temperature.

In order for this new material to find applications in chemical process equipment, it must be shown to possess chemical stability in the presence of industrial solutions. Clearly, in terms of any chemical inertness there are two components to consider: firstly, the matrix must be resistant to attack by the species in question, and secondly, the zirconia reinforcement phase must exhibit a satisfactory degree of inertness and stability. The behaviour of monolithic zirconia in supersaturated steam has been well documented [11–17]; a loss of strength in these high-temperature (> 80 °C) aqueous environments is observed in yttria-stabilized zirconias in relatively short times (50–100 h). This degradation is associated with the tetragonal (t) to monoclinic (m) transformation in the zirconia, although the mechanism of degradation is not yet fully understood. The authors have recently shown that ageing in a simulated body environment for long periods (6–24 months) at low temperatures (37 °C) also leads to a degradation in strength [18]. Similarly, there is a wealth of information available on the corrosion resistance of aluminas [19–24]. In general it has been found that aluminas exhibit excellent corrosion resistance, and by careful control of the composition they are able to withstand most aggressive environments.

However, there is a shortage of published data on the effects of long-term ageing in liquids at room

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TABLE I Effect of testing in solutions on the MOR.

Testing environment	Modulus of rupture, MOR (MPa)		
	ZTA	D995	H880
Silicone oil	500 ± 99 (1)*	296 ± 13 (1)	316 ± 52 (1)
Air	461 ± 61 (0.92)	287 ± 32 (0.97)	291 ± 36 (0.92)
Distilled water	455 ± 98 (0.91)	225 ± 28 (0.76)	270 ± 31 (0.85)
Ethylene glycol solution, 20 °C	456 ± 71 (0.91)	245 ± 24 (0.83)	256 ± 6 (0.81)
Ethylene glycol solution 80 °C	410 ± 66 (0.82)	224 ± 14 (0.76)	240 ± 25 (0.76)
20 vol% HCl	452 ± 79 (0.79)	227 ± 10 (0.77)	228 ± 69 (0.72)

*MOR normalized to silicone oil values are given in the parentheses.

temperature on the properties of ZTA. In Part I of this study [25] it was shown that the zirconia particles readily undergo the t to m transformation on ageing in HCl solutions. The extent of the transformation and the depth to which it had occurred were a function of HCl concentration and time of ageing. This paper reports the effects of various liquid environments on the mechanical properties of ZTA and two aluminas. The mechanical properties have been determined after immersion in the liquids and after periods of ageing of up to 2 years. The degradation in mechanical properties is correlated with the structural changes reported in Part I [25].

2. Experimental procedure

2.1. Materials and ageing conditions

The materials were as described in Part I, namely: ZTA (Deranox 995T); a high-purity alumina which corresponded to the matrix of the ZTA (Deranox 995); and a debased alumina (Hilox 880). The liquid environments were also the same as those employed in Part I with the addition of silicone oil for selected tests. All mechanical tests were carried out at room temperature, as were all the ageing experiments with the exception of ethylene glycol solution which was also investigated at 80 °C.

2.2. Mechanical testing

Strength (modulus of rupture), Weibull modulus, fracture toughness and crack velocities were measured as soon as possible after immersion in the liquid environments used for the ageing experiments in order to ascertain whether the environment had an 'instantaneous' effect on properties. In addition, the strength and toughness were determined as a function of ageing time; the tests were also carried out in the ageing environment.

2.2.1. Modulus of rupture testing (MOR)

All MOR tests were carried out in three-point bending, with a span of 24 mm ($L/d = 8$) and a crosshead speed of 1 mm min^{-1}. MOR specimens were 3 × 3 × 32 mm and the tensile face was polished to a 6 μm finish, and the edges bevelled to 45°.

In most cases, at least five tests were used to determine a mean value for MOR, and 20 tests for the Weibull modulus. The latter was obtained using two estimators for the probability, P_s

$$P_s = 1 - i/N + 1, \quad P_s = 1 - (i - 0.5)/N \qquad (1)$$

where i is the rank position and N is the total number of samples tested.

2.2.2. SENB fracture toughness testing

The single edge-notched bend (SENB) specimens were of nominal dimensions 4 × 3 × 32 mm, and the tensile surface was diamond-ground to a 200 grit finish. The notch was cut in the centre of the specimens prior to ageing, with a fine diamond saw (notch width 0.15 mm, depth 0.75 mm).

2.2.3. Slow crack growth measurements (double torsion)

Double torsion (DT) tests were undertaken in liquid environments in order to determine crack velocities. The specimens were 1-mm-thick flat plates, surface ground on both faces, and of nominal dimensions 25 × 100 mm. A notch (width 1 mm, length 15 mm) was used to start the crack, but tests were carried out without the aid of a guide groove for the crack. A stress relaxation technique was employed which enables the crack velocity to be determined as a function of the stress intensity from the expression proposed by Quinn [26]

$$V = (\dot{y}/B)\,(L_0/\dot{L}_0)\,(\dot{L}_1/L_1^2) \qquad (2)$$

where $\dot{y}$ is the crosshead speed; B a geometric constant ($B = 3\,Wm^2/Wt^3G$); G is the shear modulus; L_0 the maximum load; $\dot{L}_0$ is the slope at the onset of relaxation, L_1 the load at any point and $\dot{L}_1$ the slope at load L_1.

3. Results

3.1. Effect of liquid environment on mechanical properties

The preliminary work involved strength testing of the materials in solution without prior ageing. It was found that the nature of the solution had an influence on the unaged MOR for all three materials (Table I).

Testing in a water-free environment (i.e. silicone oil) resulted in the highest-recorded MOR. Aqueous solutions led to a decrease in the ambient temperature MOR, compared with values in silicone oil and air, for

TABLE II Effect of testing in liquid environments on the fracture toughness.

Environment	Fracture toughness (K_{Ic}) (MPa $\mathrm{m}^{1/2}$) ZTA	D995	H880
Silicone oil	7.2 ± 2 (1)*	3.7 ± 0.2 (1)	4.3 ± 0.2 (1)
Air	6.5 ± 0.3 (0.90)	3.8 ± 0.2 (1.02)	4.3 ± 0.1 (1)
Distilled water	5.9 ± 0.2 (0.82)	3.6 ± 0.7 (0.97)	3.6 ± 0.4 (0.84)
Ethylene glycol solution 20 °C	6.5 ± 0.5 (0.90)	3.6 ± 0.2 (0.97)	3.6 ± 0.2 (0.84)
Ethylene glycol solution 80 °C	5.5 ± 0.5 (0.76)	3.1 ± 0.2 (0.84)	3.1 ± 0.2 (0.72)
20 vol % HCl	5.8 ± 0.3 (0.81)	3.6 ± 0.2 (0.97)	3.6 ± 0.3 (0.84)

*K_{Ic} normalized to silicone oil valves are given in the parantheses.

the three materials. The normalized values also indicate that there is no relation between the nature of the solution and the instantaneous room temperature strength decrement, which was common for all three materials (except perhaps that the HCl tended to give a large decrement). The tests in ethylene glycol at 80 °C produced a further decrease in strength over tests undertaken at ambient temperature in the same liquid for all materials.

There was also a reduction in toughness in liquid environments compared to the values in silicone oil and air, although the fractional changes with respect to silicone oil tended to be smaller than those observed for strength (Table II). Nevertheless, the trends shown by toughness were similar to those previously noted for strength in that (i) tests in ethylene glycol at 80 °C led to a bigger decrement than those at room temperature; and (ii) there was no relationship with respect to the different environments at room temperature, which was common to the three materials.

The Weibull modulus, m, was determined for materials D995 and ZTA, in each of the solutions used. As shown in Table III, m is not significantly influenced by the non-acidic environments used in the present study. However, the Weibull modulus for both materials was lowest when tested in the 20 vol % HCl solution, indicating that the solution 'activated' or produced a wider range of flaws.

The effects of liquid environments on slow crack growth, as determined by the double torsion stress relaxation technique are shown in plots of log velocity against K_{I} (Fig. 1). These plots were linear in accordance with the commonly used equation for velocity, V

$$V = \alpha K_1^n$$

where α and n are constants and K_1 is the stress intensity factor. As can be seen by the best-fit lines, ZTA generally exhibited higher values for the exponents n compared to the alumina (Table IV). For both materials, the lowest value was obtained from the tests undertaken in ethylene glycol solution.

TABLE III Weibull modulus data for ZTA and D955A showing the effects of testing environment and the probability estimator employed.

Material	Environment	Weibull modulus, m $P_s = (i - 0.5/n)$	$(i/n + 1)$
ZTA	Air	9.0	7.7
	Distilled water	9.7	8.4
	Ethylene glycol, 20 °C	8.9	8.3
	20 vol % HCl	6.0	5.3
D995	Air	10.4	9.1
	Distilled water	9.1	8.1
	Ethylene glycol, 20 °C	12.4	11.0
	20 vol % HCl	4.6	4.0

TABLE IV Variation in the exponent n as a function of testing environment for stress-relaxation double-torsion tests.

Material	Environment	n
ZTA	Distilled water	103
	Ethylene glycol (20 °C)	48
	20 vol % HCl	135
D995A	Distilled water	89
	Ethylene glycol (20 °C)	59
	20 vol % HCl	73

3.2. Effect of ageing in liquid environments on mechanical properties

The effects of long-term ageing on the MOR are shown in Figs 2–4 for D995, ZTA and H880, respectively. It is apparent that for all materials the only solution to produce any significant effect on the MOR was HCl. Similarly, Figs 5–7 show the effects of ageing on the fracture toughness: again the only significant variation was observed in the HCl solution. As far as the 20 vol % HCl data are concerned, it is clear that the fastest rate of degradation occurs during the first month of ageing. The study was therefore extended to examine in more detail the effects of HCl concentration at ageing times of 1 month and less. The results are presented in Fig. 8; there was no evidence to suggest that the degradation in strength was significantly influenced by concentration for ageing times between 1 week and 1 month.

4. Discussion

4.1. Strength and fracture toughness

It has been reported [27, 28] that the strength of a ceramic is reduced in the presence of a liquid environment. The results of this study are in agreement with this view. MOR values were shown to be dependent on the nature of the testing medium. Tests undertaken in a "dry" environment (silicone oil) exhibited the highest MOR for all three materials. Testing in air produced a decrease in MOR, although the strength

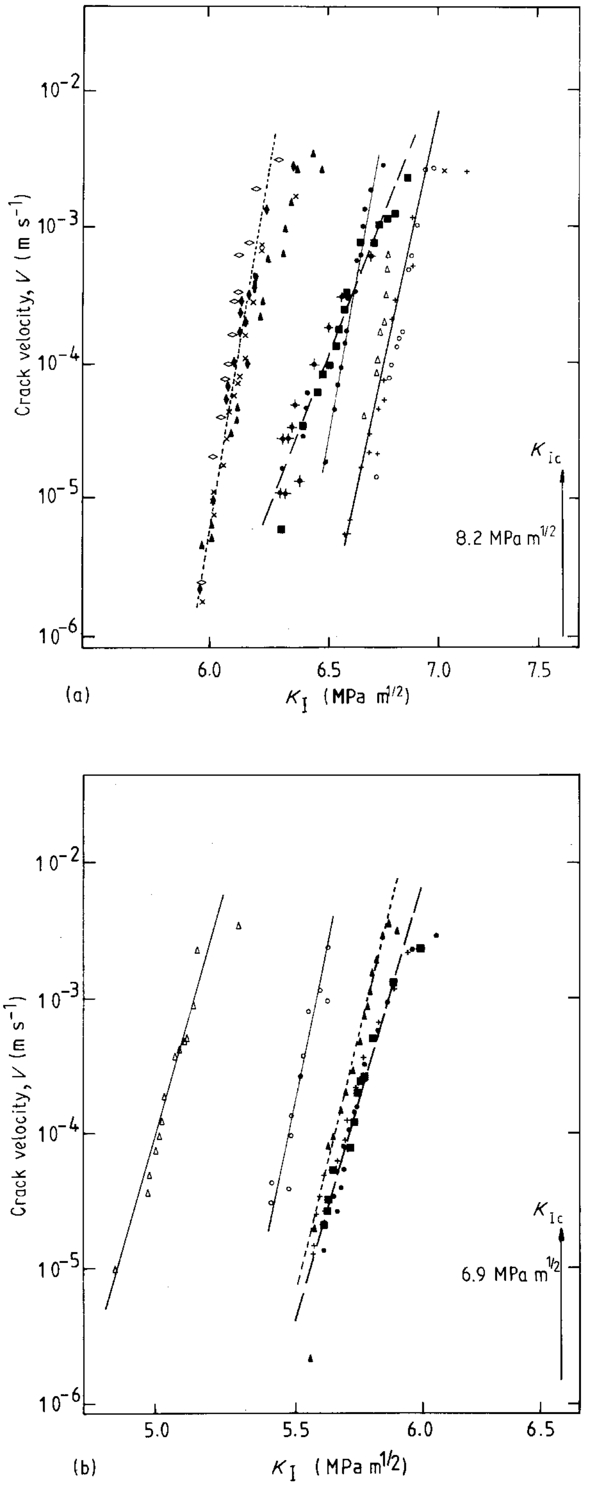

Figure 1 (a) K–V plots for ZTA tested in 20 vol % HCl (△, ○, +), ethylene glycol solution (■, ● ⧫) and distilled water (◇, ◆, ×, ▲). The different data points correspond to various loading cycles for two different test specimens. Least-squares best-fit lines. (b) K–V plots for D995A tested in 20 vol% HCl (△, ○), ethylene glycol solution (■, +, ●) and distilled water (▲). The different data points correspond to various loading cycles for two different test specimens. Least-squares best-fit lines.

was still higher than for those tests undertaken in aqueous environments. The tests in aqueous solutions produced a decrease in strength of $\simeq 10\%$ for ZTA and $\simeq 20\%$ for the aluminas, compared to values in silicone oil. The fracture toughness of all the materials followed similar trends to those exhibited by strength. These data were determined for instantaneous tests,

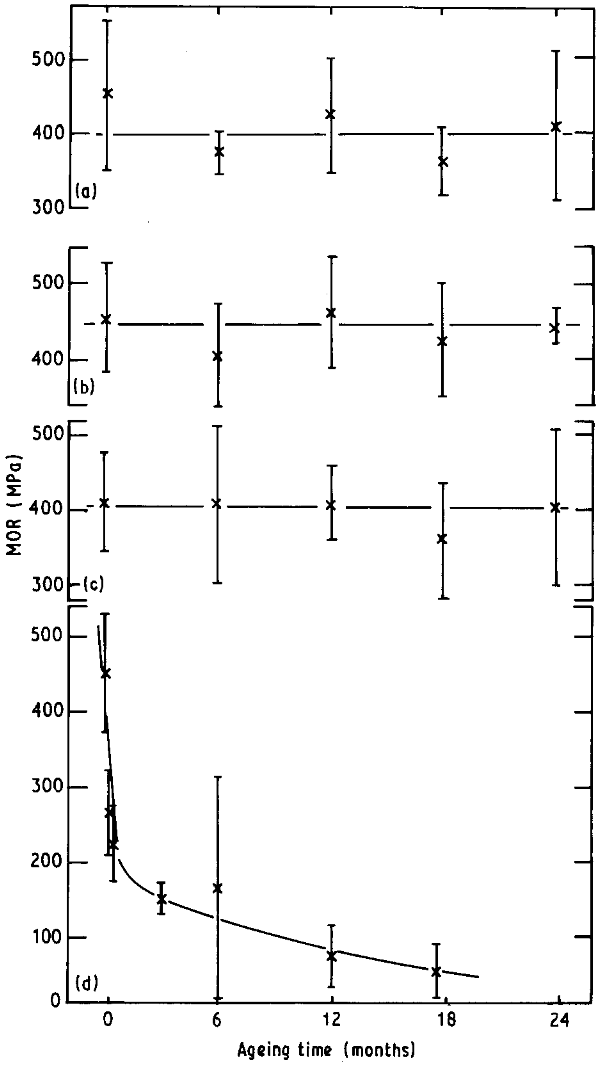

Figure 2 Effect of ageing in liquid environments on the MOR of ZTA. (a) Distilled water; ethylene glycol solution at (b) 20 °C and (c) 80 °C; (d) 20 vol% HCl.

and therefore the degradation process could not be explained by a conventional corrosion mechanism. It was concluded that a crack-tip phenomenon was responsible for the degradation. McMahon [20] attributed the mechanism to the presence of water, and certainly the strength data from this study suggest that the measured MOR decreases with increasing water content.

A further parameter to consider is the pH of the solution. Obviously, for the long-term corrosion resistance pH is very important. For example, in the case of aluminas lower-purity materials commonly contain an intergranular glass phase which, depending on composition, will be soluble in either acidic or basic solutions. In terms of the instantaneous decrease in mechanical properties (Tables I and II) it appears that in most cases the HCl solution has the most effect on mechanical properties.

4.2. Sub-critical crack growth

It has been reported for alumina ceramics [19] that the slow crack growth is controlled by the nature of the testing environment and the composition of the alumina. For example in a 99.5% alumina, the crack

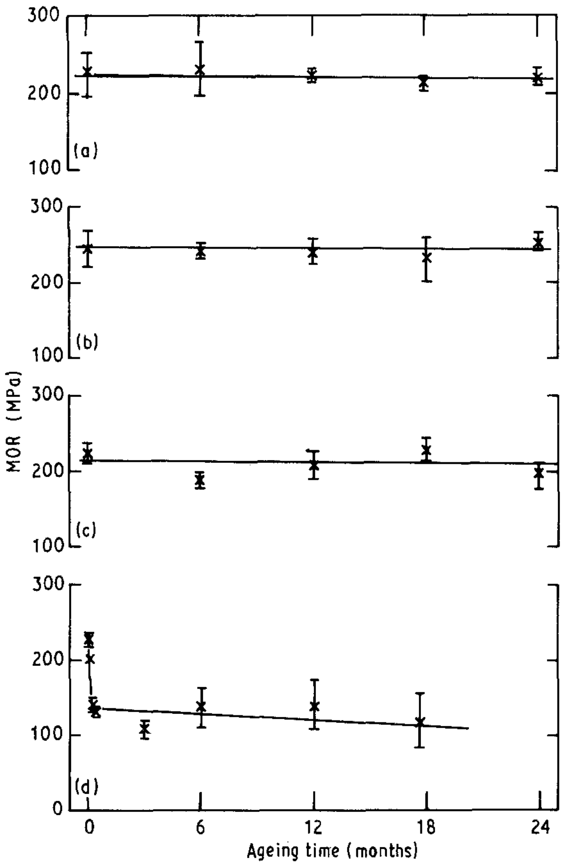

Figure 3 Effect of ageing in liquid environments on the MOR of D995A. (a) Distilled water; ethylene glycol solution at (b) 20 °C and (c) 80 °C; (d) 20 vol% HCl.

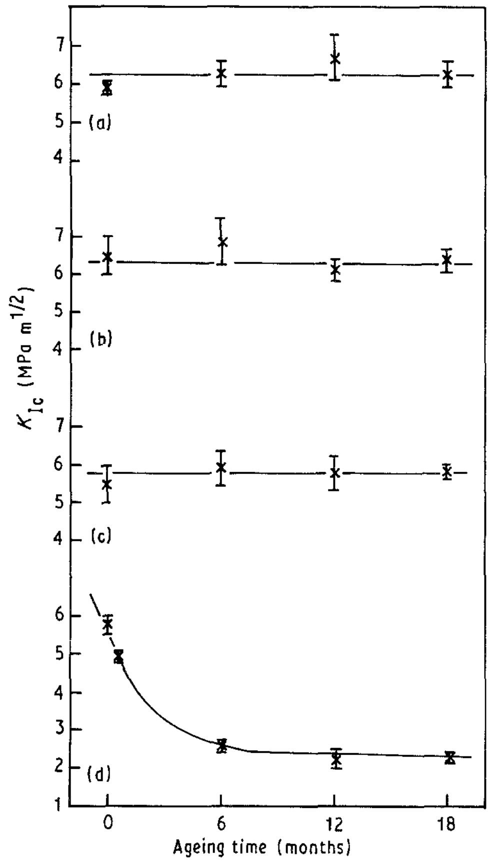

Figure 5 Effect of ageing in liquid environments on the K_{Ic} of ZTA. (a) Distilled water; ethylene glycol solution at (b) 20 °C and (c) 80 °C; (d) 20 vol % HCl.

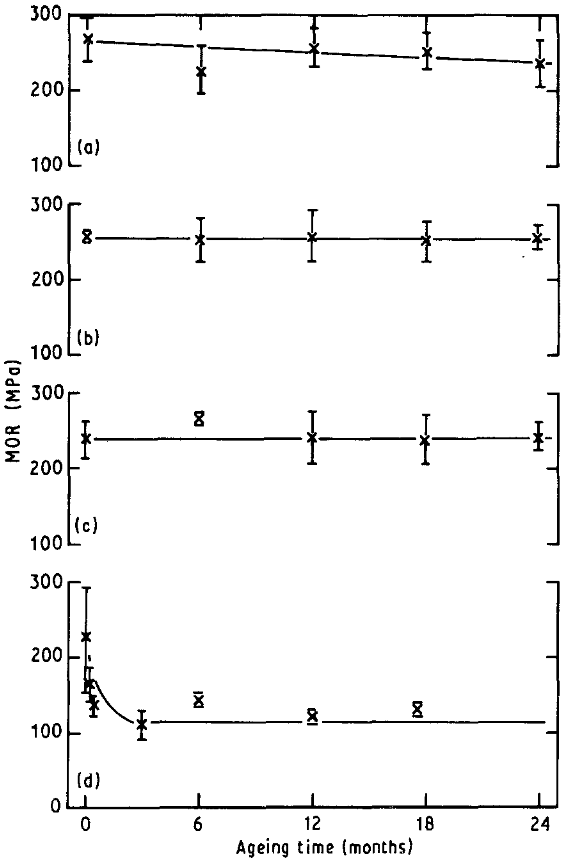

Figure 4 Effect of ageing in liquid environments on the MOR of H880A. (a) Distilled water; ethylene glycol solution at (b) 20 °C and (c) 80 °C; (d) 20 vol% HCl.

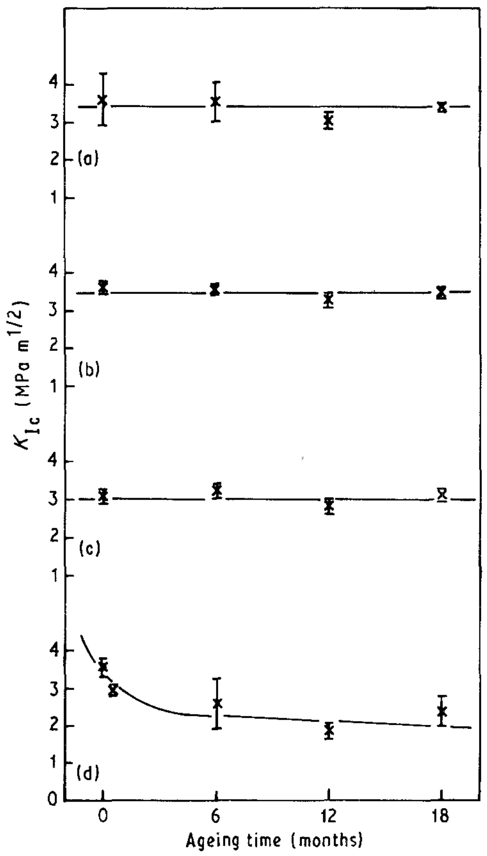

Figure 6 Effect of ageing in liquid environments on the K_{Ic} of D995A. (a) Distilled water; ethylene glycol solution at (b) 20 °C and (c) 80 °C; (d) 20 vol% HCl.

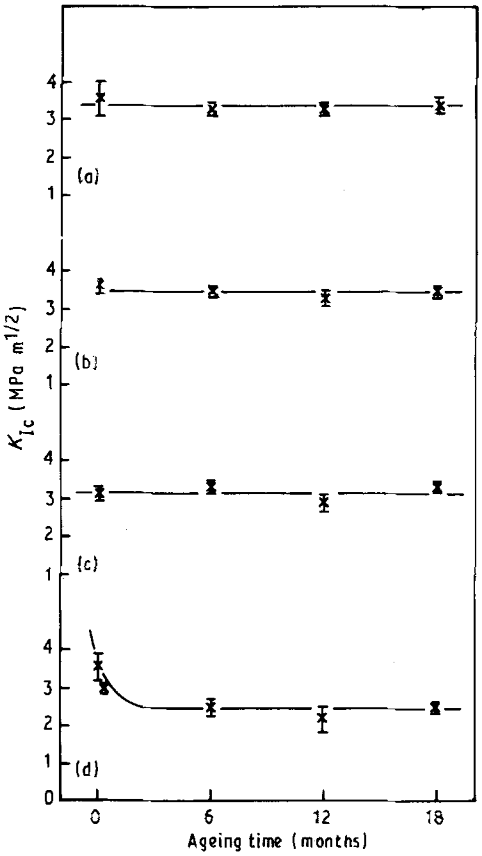

Figure 7 Effect of ageing in liquid environments on the K_{Ic} of H880A. (a) Distilled water; ethylene glycol solution at (b) 20 °C and (c) 80 °C; (d) 20 vol % HCl.

velocity will be greater, for any given stress intensity factor, for tests in water compared to air or oil [21]. The K_I–V plots for alumina obtained in the present work conformed to the conventional trend: the less aggressive the environment, the greater the value of K_I required to produce a given V. However for ZTA the opposite effect was exhibited, and testing in hydrochloric acid produced the highest value of K_I for any given crack velocity. It is suggested that this effect is a result of transformation toughening. It has already been established that there is a back stress on the crack faces associated with the t → m transformation, and this can serve to increase the crack resistance of the material with crack length; this is commonly termed wake toughening. Other wake toughening mechanisms may be operative in nominally single-phase ceramics such as alumina. Wake toughening leads to what is known as a "R-curve behaviour" which has been observed in both alumina and zirconia materials [3, 7, 29–31].

If one considers the slow crack growth of ZTA in the presence of HCl, as the crack propagates the conventional transformation toughening mechanism will operate. In addition to this, the HCl will increase the degree of transformation by a chemical means [25, 32]. Thus there are two effects: (i) an increased resistance to crack propagation as the crack grows due to traditional transformation toughening; and (ii) the HCl will induce further transformation both ahead of and behind the crack by chemical attack, the additional transformation causing an increase in the compressive stress and thus providing a further incremental increase in crack resistance.

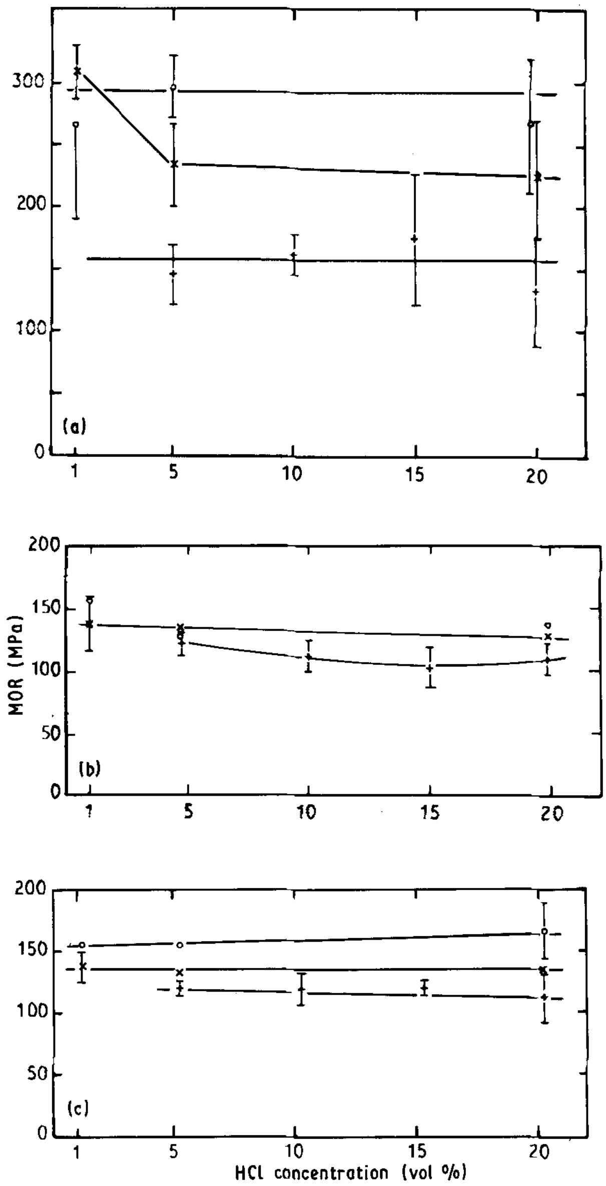

Figure 8 Effect of HCl concentration and ageing time on the MOR of (a) ZTA; (b) D995A; (c) H880A. (○) 1 week; (×) 2 weeks; (+) 1 month.

The combined effect of (i) and (ii) will enhance the resistance to further crack propagation and hence the stress intensity factor will increase for any given crack velocity.The ranking of the K_I-V curves for ZTA suggests that HCl was a less aggressive solution than distilled water. However, from the findings of the long-term ageing experiments, this is evidently not the case, as the acid solution produces a degradation in both strength and toughness after ageing for as short a time as 24 h.

The slow crack-growth exponent, n, is usually considered to be an important parameter in determining the lifetime of a component in service as the time T_s for failure at a service stress of σ_s is related to the time to failure T_0 at a reference stress σ_0 by [33]

$$(\sigma_0/\sigma_s)^n = T_s/T_0 \qquad (3)$$

It follows that the larger the value of n, the greater the resistance to slow crack growth. In the case of alumina, the values obtained in the present work varied from 59 to 89 depending on the solution. These values are similar to the values obtained by other workers for aluminas in various solutions, namely 17–100 [28]. The *n* value of 135 for ZTA in 20% HCl is high and suggests long lifetimes in this environment. However this analysis is usually applied to ceramics which are relatively stable in the environment under investigation, such that the results of the short term tests used to determine *n* may be employed to predict behaviour under small stresses for long times. In the case of ZTA in HCl, the structural changes are sufficient to cast doubt on the reliability of using *n* from the DT tests in predicting lifetimes from Equation 3. In contrast, the extent of the t → m transformation in water at room temperature is negligible, and it may be valid to predict lifetimes; the relative values of *n* in distilled water for ZTA and alumina were 103 and 89, respectively, which indicates a superior service performance for ZTA.

4.3. Long-term ageing

There was no significant variation in either MOR or fracture toughness after ageing ZTA, D995 and H880 in distilled water and ethylene glycol solution (20 and 80 °C) for 24 and 18 months, respectively (Figs 2–4 and 5–7). From other work on zirconia ceramics aged in water at elevated temperatures [12, 16, 17], one might have expected to see a degradation in properties for ZTA after ageing for 2 years in ethylene glycol solution at 80 °C. However, the results in Part I of this study show that after 2 years of ageing, the monoclinic content was only 32.5%, considerably less than predicted from previous work [16] at elevated temperatures in zirconia. It was suggested that the corrosion mechanism in ethylene glycol solution was essentially the same as found for zirconia in aqueous solutions, but was inhibited to a certain extent by the ethylene glycol. The absence of any strength degradation may be accounted for by the relatively low monoclinic content and the negligible depth of penetration; the latter point will now be discussed further when considering the strength degradation in HCl solutions.

Ageing all three materials in 20 vol % HCl had a marked effect on both the MOR and fracture toughness, especially for ZTA. The degradation was so dramatic that ageing times were reduced, and tests carried out for periods as short as 24 h. The MOR of ZTA decreased by 18% after ageing for 24 h in 20 vol % HCl, and exhibited an 86% decrease after 18 months. In comparison the MOR of D995A decreased by 12% after 24 h, but only 37% after 18 months. Similarly the fracture toughness decreased by 65% after ageing ZTA for 18 months, compared with a decrease of only 33% for D995A and H880A.

In Part I, it was shown that the monoclinic content in the ZTA aged in distilled water and ethylene glycol solution (20 °C) had not increased. This is consistent with there being no evidence of any loss in mechanical performance in these solutions, as it is generally accepted that degradation is a consequence of the formation of the monoclinic phase. In contrast, examination of the specimens aged in HCl showed a gradual increase in monoclinic content from 15.5% after ageing for 24 h to 56% for 6 months; it should be noted that for extended ageing times beyond 6 months there was no further increase in the monoclinic content. There appeared to be no relationship between HCl concentration and the proportion of monoclinic phase for specimens aged for up to 3 months. Even for ageing times as short as 24 h, there was little variation in the degree of transformation for concentrations between 1 and 20 vol % HCl (see Table IV, Part I) [25].

The depth to which the HCl attacked the ZTA was found to increase with increasing ageing time, with complete penetration to a depth of 1.5 mm occurring after 3 months. Unlike the monoclinic content, the depth of attack was influenced by the concentration of HCl: as the concentration increased the depth of attack increased (see Table V, Part I) [25].

Clearly the mechanical properties after ageing may be determined by either the percentage monoclinic phase or the depth to which it has been formed (depth of attack), or some combination of these. As shown in Fig. 9, the plot of MOR against the proportion of monoclinic zirconia may be considered to have two distinct linear regions. Similarly, the relationship between MOR and depth of penetration was not simple, as illustrated in Fig. 10. Sato *et al.* [14] suggested that the strength of TZP materials was controlled not by the degree of transformation, but by the depth of the transformed layer. From the present study it is difficult to say which of the two is the most important factor in controlling strength: the two are interrelated, as shown in Fig. 11. The monoclinic content increased with increasing depth of attack; however, on complete penetration the monoclinic content increased further until it reached 60%, which appears to be the maximum monoclinic content of the system. Full penetration occurred after ageing for 3 months, although the strength continued to fall for longer ageing periods. Therefore the increase in monoclinic content must play some role.

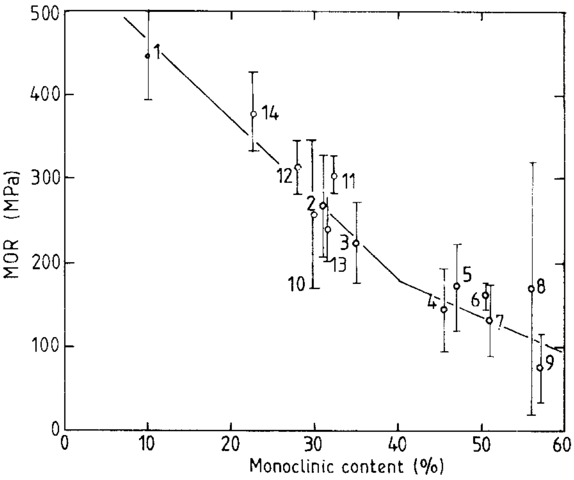

Figure 9 Relationship between MOR and monoclinic content for ZTA aged in HCl. Ageing time and HCl content: 1, unaged; 2, 1 week, 20%; 3, 2 weeks, 20%; 4, 3 months, 5%; 5, 3 months, 15%; 6, 3 months, 10%; 7, 3 months, 20%; 8, 6 months, 20%; 9, 12 months, 20%, 10, 1 week, 1%; 11, 1 week, 5%; 12, 2 weeks, 1%; 13, 2 weeks, 5%; 14, 24 h, 20%.

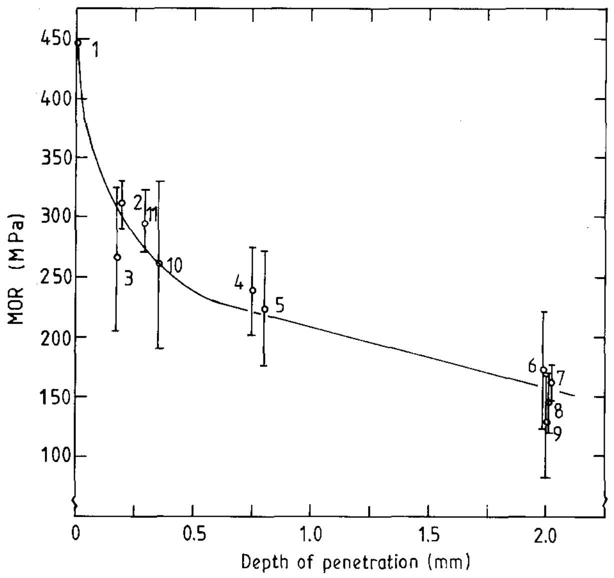

Figure 10 Plot of MOR against depth of penetration for ZTA aged in HCl Ageing time and HCl content: 1, unaged; 2, 2 weeks, 1%; 3, 1 week, 20%; 4, 2 weeks, 5%; 5, 2 weeks, 20%; 6, 3 months, 15%; 7, 3 months, 10%; 8, 3 months, 5%; 9, 3 months, 20%; 10, 1 week, 1%; 11, 1 week, 5%.

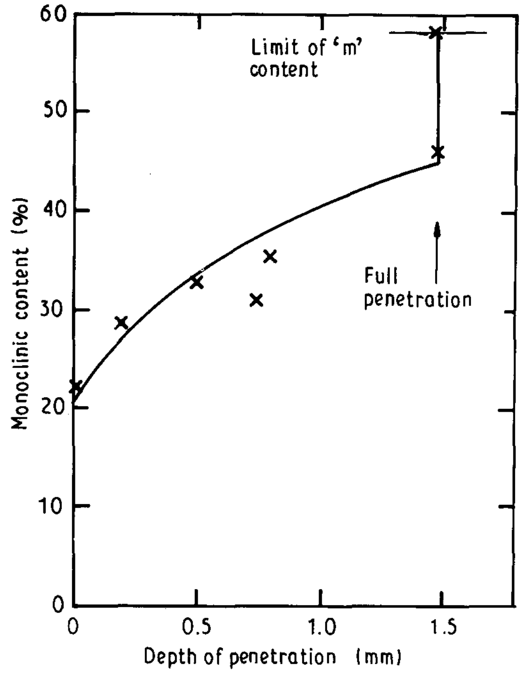

Figure 11 Monoclinic content against depth of attack for ZTA aged in HCl. Note complete penetration is reached prior to the monoclinic content reaching a maximum.

However, if one considers the behaviour of ZTA in ethylene glycol solution (80 °C), there was an increase in monoclinic content on ageing but the strength remained unchanged and there was negligible penetration of the liquid into the body of the ZTA. This would tend to suggest that the conclusion drawn by Sato *et al.* [14] for zirconias is also valid for ZTA, and that the strength is primarily controlled by the depth of the transformed layer and not the degree of transformation.

5. Conclusions

1. Aqueous liquid environments reduced the 'instantaneous' strength and toughness with respect to the values in silicone oil and air for all the ceramics investigated. The Weibull modulus was less in 20% HCl than in other environments.

2. The slow crack growth of ZTA did not conform to the conventional format, as followed by alumina: the most corrosive environment, HCl, required an increased stress-intensity factor for a given crack velocity. This was thought to be caused by the interaction of HCl with zirconia at the crack tip and in the crack wake, leading to the t → m transformation.

3. Formation of the monoclinic phase on ageing ZTA in HCl solutions resulted in a loss of strength and toughness. Both the monoclinic content and the depth of penetration play a role in determining strength, but it is suggested that the depth of penetration is more important.

6. Acknowledgements

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