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Effects of liquid environments on zirconia-toughened alumina

Part I *Chemical stability*

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The structural changes which occur in zirconia-toughened alumina when aged in a range of liquid environments (distilled water, ethylene glycol solution and HCl at room temperature, and ethylene glycol solution at 80 °C) is described. The changes were monitored by X-ray diffraction, surface analysis, analysis of the ageing solutions and microstructural observations. It was found that HCl induced significant proportions of the zirconia particles in the zirconia-toughened alumina to transform from the tetragonal to the monoclinic crystal structure. This transformation was accompanied by microcracking which eventually led to macrocracking after long periods of ageing. The transformation is a consequence of the leaching of the yttrium from the zirconia particles, thereby reducing their stability.

1. Introduction

Previous workers [1–4] have observed a degradation in the properties of zirconia ceramics after ageing in the presence of water vapour at elevated temperatures, e.g. ≃ 200 °C for relatively short times of typically less than 120 h. However, the effects of ageing of zirconias and zirconia-toughened aluminas (ZTAs) in aqueous solutions (neutral or acidic) at room temperature have not been reported.

Recently the authors [5] have demonstrated that long-term ageing of yttria-stabilized zirconias and a ZTA in a simulated body solution at 37 °C results in some transformation to the monoclinic polymorph and a reduction in mechanical performance. As far as acidic solutions are concerned, a 30% sulphuric acid solution at 63 °C has been found to cause cracking in yttria partially-stabilized zirconias but no degradation was found after 150 h at 41 °C, which was the lowest temperature investigated [6]. Part II of this work [7] reports the mechanical properties of ZTA, a high-purity alumina (D995) and a debased alumina (H880) after long-term ageing in various solutions. There was no evidence of a degradation in strength or fracture toughness after ageing in distilled water or ethylene glycol solution at 20 or 80 °C for periods up to 24 months for the strength specimens and 18 months for the fracture toughness tests. However, ageing in 20 vol % hydrochloric acid had a marked effect on the strength and toughness of all three materials, but particularly for ZTA. The effect was evident for ZTA after ageing for periods as short as 24 h, and for short ageing periods of up to 1 month the concentration of the HCl, in the range 1–20 vol %, was not significant [7].

The results of the experiments undertaken to understand the structural changes which occur in ZTA on ageing in liquid environments are described. Particular emphasis is paid to the effect of HCl; the structural data obtained are correlated with the degradation in mechanical properties in Part II [7].

2. Experimental procedure

2.1. Material and ageing conditions

The study was performed on three materials supplied by Morgan Matroc Ltd*, namely a debased alumina (Hilox 880), a high-purity alumina (Deranox 995) and a zirconia-toughened alumina (Deranox 995T), details of which are given in Table I. The three materials were aged in a range of liquid environments for appropriate periods of up to 2 years as specified in Table II.

2.2. Crystallographic changes

The volume fraction, X_m, of the monoclinic phase with respect to the total zirconia content was determined from X-ray diffraction (XRD) data obtained using a diffractometer with CuK_α radiation and the following expression proposed by Fillit *et al.* [8]

$$X_m = \frac{C[I(1\,1\,\bar{1})_m + I(1\,1\,1)_m]}{C[I(1\,1\,\bar{1})_m + I(1\,1\,1)_m] + I(1\,1\,1)_t} \quad (1)$$

where I is the intensity and $C = 1.381$ for CuK_α radiation.

$$C = R(1\,1\,1)_t/[R(1\,1\,\bar{1})_m + R(1\,1\,1)_m] \quad (2)$$

where $R(\mathrm{h\,k\,l})_I$ is the theoretical line intensity, and the subscripts m and t refer to the monoclinic and tetragonal phases, respectively.

XRD analysis was undertaken on the polished surfaces of ZTA specimens. The diffractometer was operated at 40 kV in step-scan mode with a 0.01° 2θ step

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TABLE I Materials employed

Material	Purity (%)	Sintering temperature (°C)	Grain size (μm)
Deranox 995	99.5% alumina	1740	16
Deranox 995T	99.5% alumina 20 wt % ZrO_2 + 3 mol % Y_2O_3	1630	3 0.5
Hilox 880	86% alumina + SiO_2, MgO, CaO	1425	4–6

TABLE II Ageing study conditions

Solution	Temperature (°C)	Time (weeks)
Distilled water	20	26, 52, 78, 104
50% ethylene glycol	20	26, 52, 78, 104
50% ethylene glycol	80	26, 52, 78, 104
20% HCl	20	26, 52, 78, 104
20% HCl	20	1, 2, 4, 13
15% HCl	20	1, 2, 4, 13
10% HCl	20	1, 2, 4, 13
5% HCl	20	1, 2, 4, 13

TABLE III Effect of ageing time and environment on the monoclinic content of ZTA

Environment	Relative monoclinic content (%)				
	Ageing time (weeks)				
	Instant	26	52	78	104
Air	10.0	–	–	–	–
Distilled water	9.5	12.0	9.0	10.0	15.5
Ethylene glycol (20 °C)	11.0	9.0	11.0	9.5	11.0
Ethylene glycol (80 °C)	12.0	21.5	21.5	21.0	32.5
20 vol % HCl	13.0	56.0	58.0	56.5	–

TABLE IV The influence of HCl concentration on the monoclinic content of ZTA aged for short periods

Ageing time	Relative monoclinic content (%)				
	HCl concentration (vol %)				
	1	5	10	15	20
24 h	15.5	10.5	15.5	15.5	22.0
1 week	29.0	32.5	–	–	31.0
2 weeks	28.5	31.0	–	–	35.5
13 weeks	–	45.5	46.5	45.5	45.0

and a count time of 1 s per step over the 2θ range 27–32° and 72–75°. The raw data were collected and processed in a microcomputer by peak smoothing, with a smoothing interval of five data points, and K_{α_2} peak stripping. The areas of the diffraction peaks were used in Equation 1 to calculate the volume fraction of the monoclinic phase.

2.3. Compositional changes

The ageing solutions were analysed using an atomic absorption spectrophotometer (AAS), at a lamp setting of 10 mA with a nitrous oxide flame. The elements under investigation were primarily Y and Zr, although the trace elements and Al were also monitored.

Secondary ion mass spectrometry (SIMS) was used to investigate changes in surface chemistry of ZTA after prolonged ageing in 20 vol % HCl. Three specimens were examined: a polished unaged surface: polished and aged for 3 months; and polished and aged for 6 months. Specimens were cleaned and degreased prior to determination of the depth profiles of Zr, Y and Al, to a depth of 1 μm.

X-ray photo-electron spectroscopy (XPS) was also employed to characterize the surface chemistry as a function of ageing. The specimens investigated were a polished unaged surface; a polished surface aged for 6 months in 20 vol % HCl; and a polished surface aged for 12 months in 20 vol % HCl. The peaks were normalized with respect to the aluminium peak area, thus allowing qualitative comparison between the peaks of the important secondary elements, namely Zr and Y.

2.4. Microscopy

Light microscopy was used to examine the degree of microcracking and associated damage of aged materials. The specimens were sectioned and mounted in cold-setting resin, and the cross section polished to a 1-μm diamond finish.

Specimens for examination in the scanning electron microscope (SEM) were prepared from fractured modulus of rupture (MOR) test pieces. The major part of the work was undertaken on fracture surfaces, although selected polished surfaces were also examined. The specimens were mounted and gold coated prior to examination, in both the back-scattered and secondary electron image modes.

The depth of attack (and hence the depth of the transformed layer) was also determined by dye-penetrant testing. The specimens were soaked in dye-penetrant for 1 h, the excess dye removed, and the sample sectioned prior to examination.

3. Results

3.1. Effect of ageing on the monoclinic to tetragonal ratio in ZTA

Table III lists the monoclinic content as a function of both ageing time and environment; as with the strength and fracture toughness data [7], it was the ageing in the HCl solution that produced the greatest change. However there was also evidence of an increase in the monoclinic content after ageing in ethylene glycol at 80 °C.

A more detailed examination of the role of HCl concentration on the monoclinic content of ZTA showed that there was little variation in monoclinic content with increasing HCl concentration, even for ageing times as short as 24 h (Table IV).

3.2. Measurement of the depth of attack of ZTA after ageing in HCl

Dye-penetrant testing of ZTA aged in HCl showed the depth to which the acid had attacked, hence the

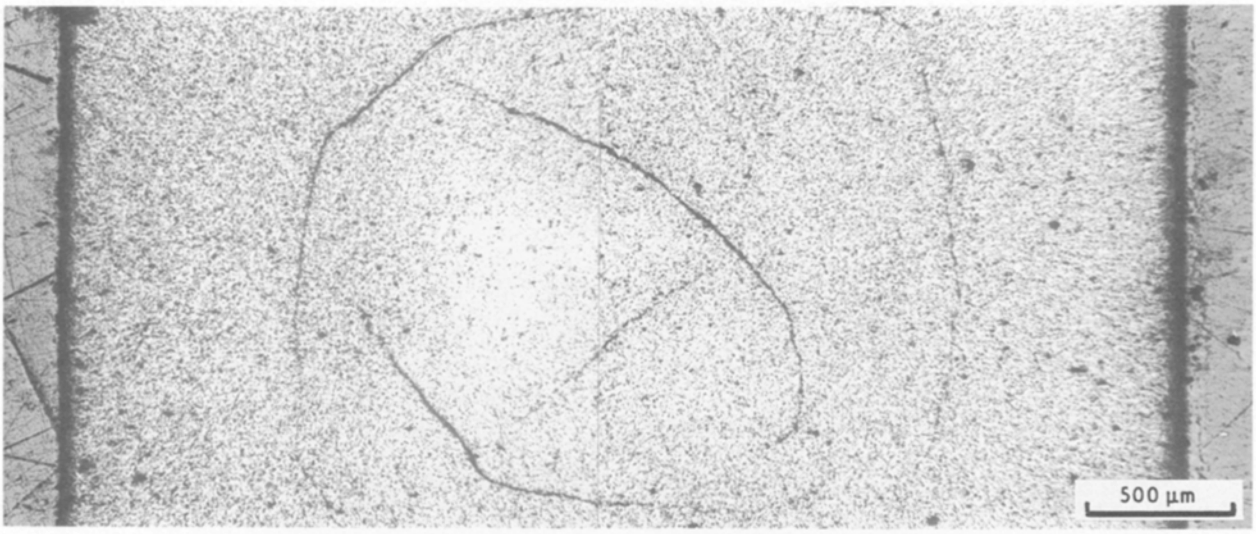


Figure 1 Optical micrograph from a polished cross section of ZTA, aged for 12 months in 20 vol % HCl. Note the extensive depth of attack and the macrocracking resulting from the coalescence of microcracks.

TABLE V Depth of penetration of dye-penetrant as a function of ageing time and HCl concentration for ZTA

Ageing conditions		Depth of penetration (mm)	
3 months	20 vol %	Complete	1.50
	15 vol %	Complete	1.50
	10 vol %	Complete	1.50
	5 vol %	Complete	1.50
2 weeks	20 vol %	Partial	0.80
	5 vol %	Partial	0.75
	1 vol %	Partial	0.20
Unaged		None	0.00

transformation depth. As shown in Table V, the depth of attack increased with increasing ageing time, with full penetration of the 3-mm-thick specimens occurring after 3 months. Also after short ageing times, as exemplified by the data at 2 weeks, the depth of penetration increases with increasing concentration.

Polished cross-sections of specimens aged in HCl were examined under a light microscope to determine the severity of attack. The results confirmed the dye-penetrant penetration data and showed that ZTA had been more severely attacked than the aluminas. Fig. 1 shows the complete cross section of a ZTA specimen which has been fully penetrated after ageing for 12 months in 20 vol % HCl; it is clear that the network of microcracks is extensive and that towards the centre of the specimen the microcracks have linked together to form macrocracks.

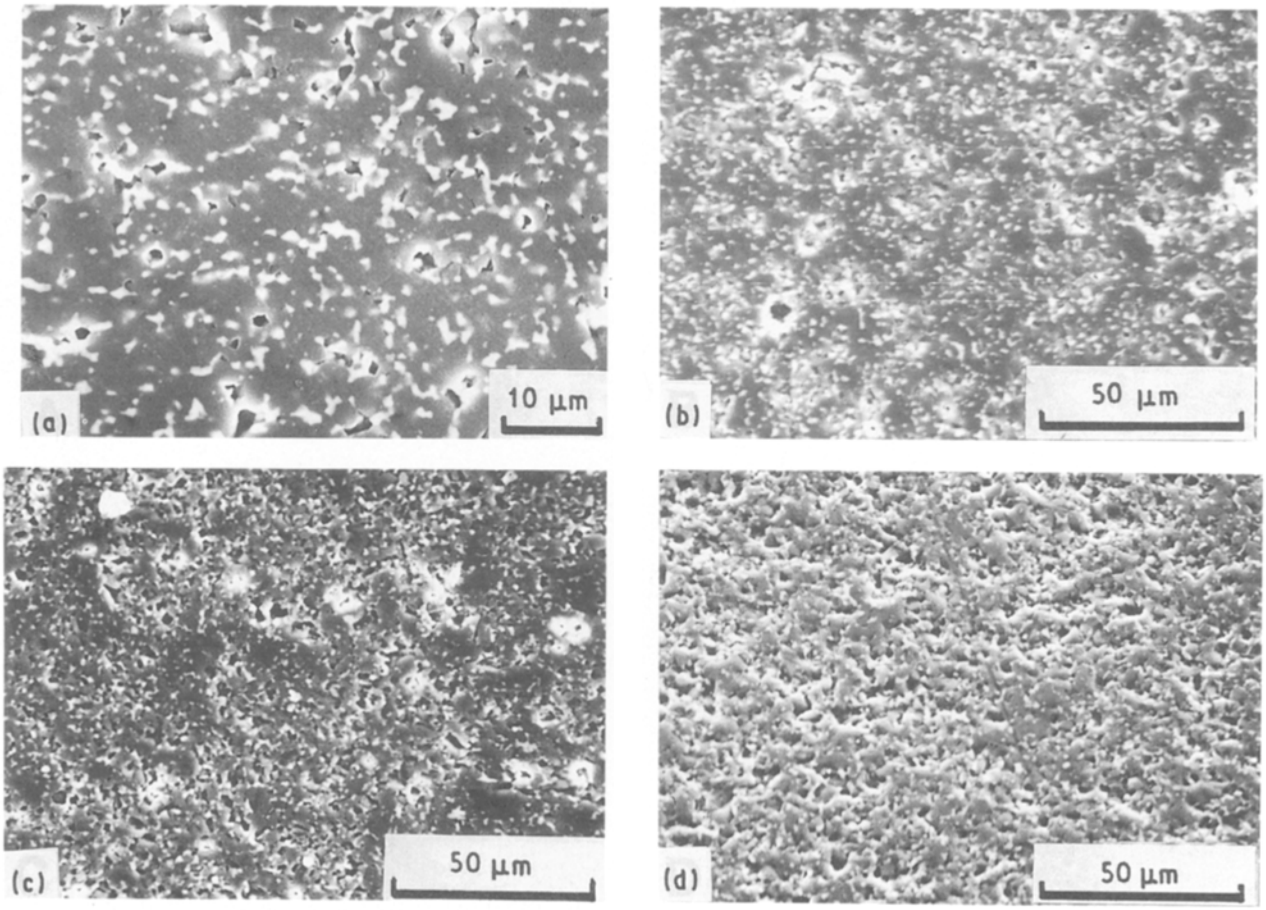
3.3. Effects of ageing on the microstructure of ZTA and D995 alumina

SEM was used to examine the polished tensile surface and the fracture face of aged MOR specimens. No difference was found when examining the fracture surfaces of all three materials after ageing in distilled water and ethylene glycol solution (at both 20 and 80 °C) for 12 months. The polished surface of ZTA exhibited more microcracking following ageing in 20 vol % HCl. Fig. 2 shows a series of five micrographs of polished surfaces of ZTA: the first is of ZTA in the as-polished condition; the second after ageing for 6 months in ethylene glycol solution at 80 °C (there is no apparent difference between (a) and (b)); the third and fourth show the microcracked surface after ageing in 20 vol % HCl for 6 and 12 months, respectively; and the fifth micrograph is a backscattered image after ageing for 12 months in 20 vol % HCl – note that the zirconia particles are still evident at the surface (the zirconia appears as the white phase).

3.4. Surface analysis of ZTA following ageing in 20 vol% HCl for up to 12 months

The three specimens examined by SIMS were unaged, and aged for 3 and 6 months; the traces of the intensities of Mg, Cl, Al and Zr to a depth of 1 µm are shown in Fig. 3a. No significant change in surface chemistry was detected with ageing in HCl from these plots. In order to improve such comparisons, the Y and Zr intensities from the unaged specimen and the specimen aged for 6 months were normalized to the Al intensity; the Y intensity was also normalized to that of Zr (Fig. 3b). The Y/Zr and Y/Al appear to decrease slightly after 6 months' ageing. However these reductions are at the reproducibility limit of the equipment and in themselves cannot be considered to be conclusive evidence of a compositional change.

XPS was also used to determine the surface chemistry of ZTA before and after ageing in 20 vol % HCl; analyses for Zr and Y were carried out, as well as for the trace elements within the alumina matrix. It must be emphasized that care is needed when comparing the peak intensities of spectra and to aid the comparison of the Y content of the surface the Y spectra plotted in Fig. 4 have all been normalized to the aluminium peak, which is assumed to remain constant. There was evidence of a depletion in the proportion of Y at the surface, whereas similar plots for Zr demonstrated that the Zr concentration remained constant after ageing for up to 12 months. Table VI



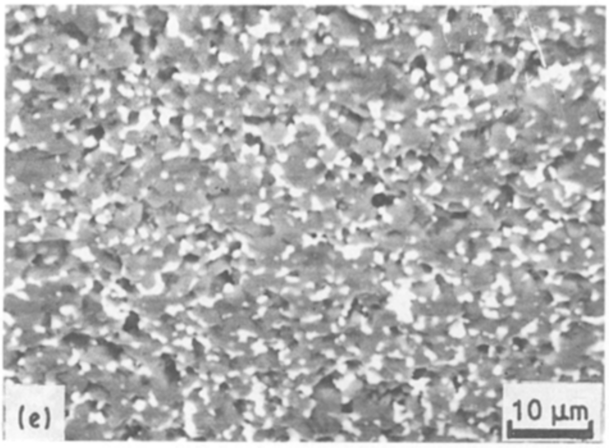


Figure 2 SEMs showing the effect of ageing on the initially polished surface of ZTA. (a) No ageing; (b) aged for 6 months in ethylene glycol solution at 80 °C; (c) aged for 6 months in 20 vol % HCl; (d) aged for 12 months in 20 vol % HCl; (e) aged for 12 months in 20 vol % HCl (backscattered electron image). Note the surface attack when aged in HCl.

summarizes the XPS results in terms of the intensities of Zr 3D and Y 3D peaks, normalized to the O 1S peak intensity (which is assumed to remain constant), for ZTA aged in 20 vol % HCl. The reduced intensity of the Y peak on ageing, which contrasts with the constancy of the Zr, is the important feature of the data.

3.5. AAS analysis of the ZTA ageing solutions

The ageing solutions were analysed, following the completion of the ageing period, by atomic absorption spectrometry (AAS). There was no significant increase in the concentration of either Zr or Y after ageing in ethylene glycol (20 and 80 °C) or distilled water. However, as shown in Fig. 5, there was an increase in the proportion of Y with increasing ageing time for ZTA aged in HCl solutions. The AAS results also demonstrated that, at the shorter ageing times, as the concentration of the HCl solution increased more Y was leached from the ceramic (Table VII). The low amount of Zr in solution after 12 months' ageing in 20 vol % HCl is also worthy of note.

4. Discussion

The above results demonstrate that the tetragonal zirconia particles in ZTA are prone to transform to the monoclinic structure on ageing in HCl solutions. HCl solutions have also been shown [7] to have a deleterious effect on strength and toughness. Clearly it is of importance to understand this "corrosive" effect of HCl solutions.

TABLE VI Peak intensities for Zr 3D and Y 3D normalized to the O 1S peak intensity

Element	As-received	Aged in 20 vol % HCl		
		3 months	6 months	12 months
O 1S	1	1	1	1
Zr 3D	0.05	0.04	0.04	0.04
Y 3D	0.05	0.008	0.007	0.007

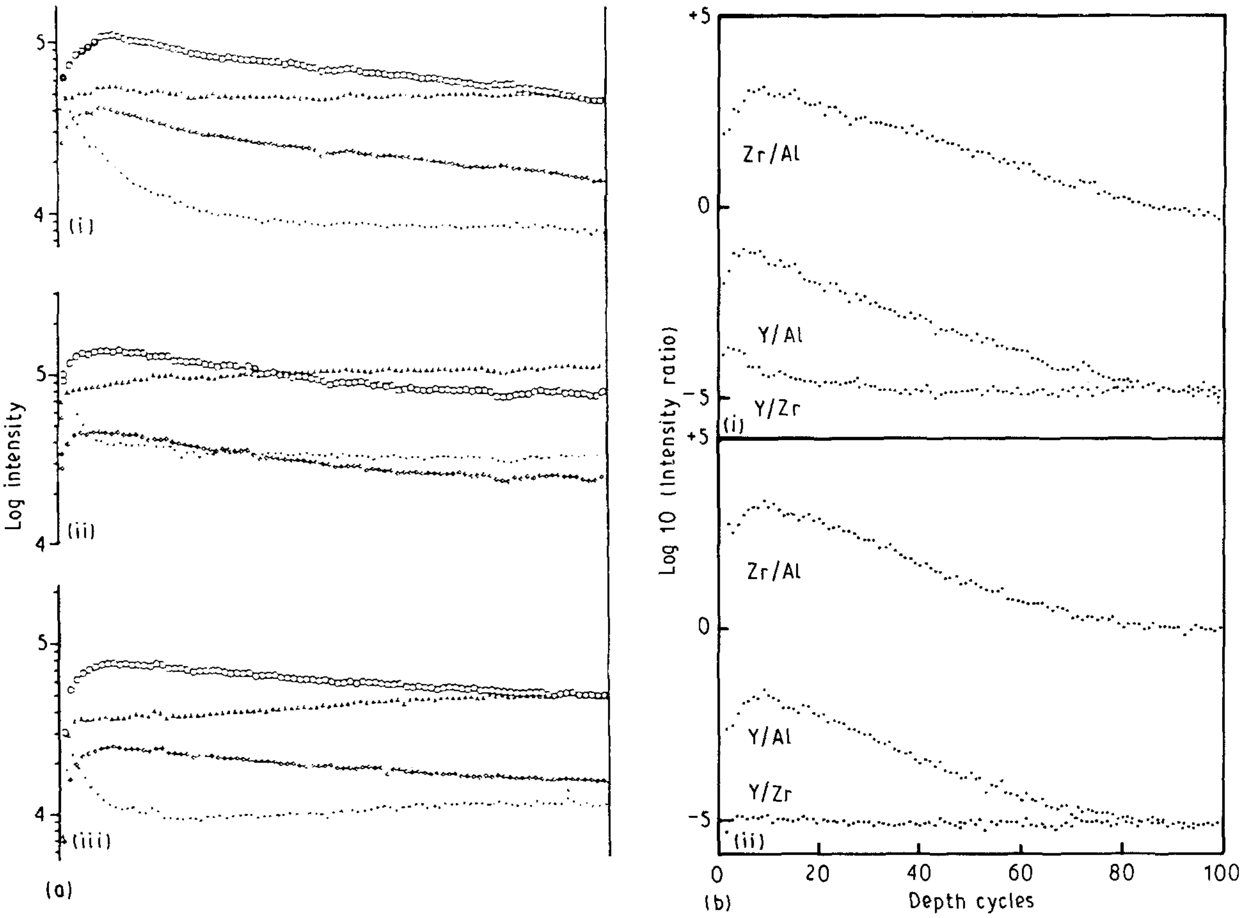


Figure 3 (a) Surface analysis (SIMS) traces for ZTA to a depth of 1 μm. (i) as-polished surface; aged in 20 vol % HCl for (ii) 3; (iii) 6 months. Note there is no significant variation in surface composition on ageing. (· · ·) Mg; (△) Al; (◇) Y; (○) Zr. (b) Surface analysis (SIMS) traces for ZTA showing the Zr/Al, Y/Al and Y/Zr ratios for ZTA in (i) as-polished condition; and (ii) aged for 6 months in 20 vol % HCl. There is a slight decrease in the Y/Zr and Y/Al ratios after ageing for 6 months.

TABLE VII Showing an increase in Y content of HCl ageing solutions after ageing ZTA for up to 3 months. At the shorter ageing times the leaching of Y is dependent on the concentration of the HCl solution

Ageing conditions		Amount of Y present (p.p.m.)
Time	HCl content (%)	
1 week	1	2.1 ± 0.9
	5	4.8 ± 1.4
	20	5.1 ± 1.0
2 weeks	1	3.4 ± 1.4
	5	4.4 ± 1.4
	20	5.1 ± 1.2
3 months	5	28.4 ± 1.3
	10	28.9 ± 0.9
	15	27.6 ± 0.5
	20	19.5 ± 1.4
12 months	20	50.0 ± 1.0
12 months	20	4.0 ± 0.5 (Zr)

In an attempt to define more closely the mechanism of attack, chemical analysis of the surface of the ZTA specimens and the ageing solutions was performed. As shown in Fig. 5 and Table VII, an increasing proportion of yttrium was detected in the ageing solution, reaching 50 p.p.m. after ageing for 12 months. Also, as the HCl concentration increased, there was an increase in the amount of yttrium leached from the ZTA. It should be noted that the yttrium measured in the solution was not associated with the dissolution of zirconia from the alumina matrix, as the total amount of zirconium detected after 12 months' ageing was only 4 p.p.m. Furthermore, the presence of zirconia on the polished surfaces of ZTA specimens aged in HCl was observed in the SEM (Fig. 2e).

It is known that yttria is highly soluble in HCl, and it is therefore proposed that the mechanism for the degradation in mechanical properties relies on the dissolution of yttrium from the zirconia. Removal of the stabilizing oxide leads to the transformation of the metastable zirconia particles to the monoclinic polymorph. Associated with the transformation will be the formation of microcracks around the particle, which in turn will uncover virgin surfaces to the corrosive media, hence promoting further leaching of yttria and the subsequent transformation and microcrack formation. Eventually the density of microcracks will be high enough for them to link together and form macrocracks, as seen in Fig. 1. It is apparent from the experimental data that both the rate of transformation to the monoclinic phase (Table IV) and the rate of solution of yttrium in the ageing solutions (Fig. 5) decrease with time. A possible explanation for this is that as the t → m transformation progresses, the compressive stress generated within the matrix places the local tetragonal particles under more constraint. Therefore as the transformation continues, it becomes

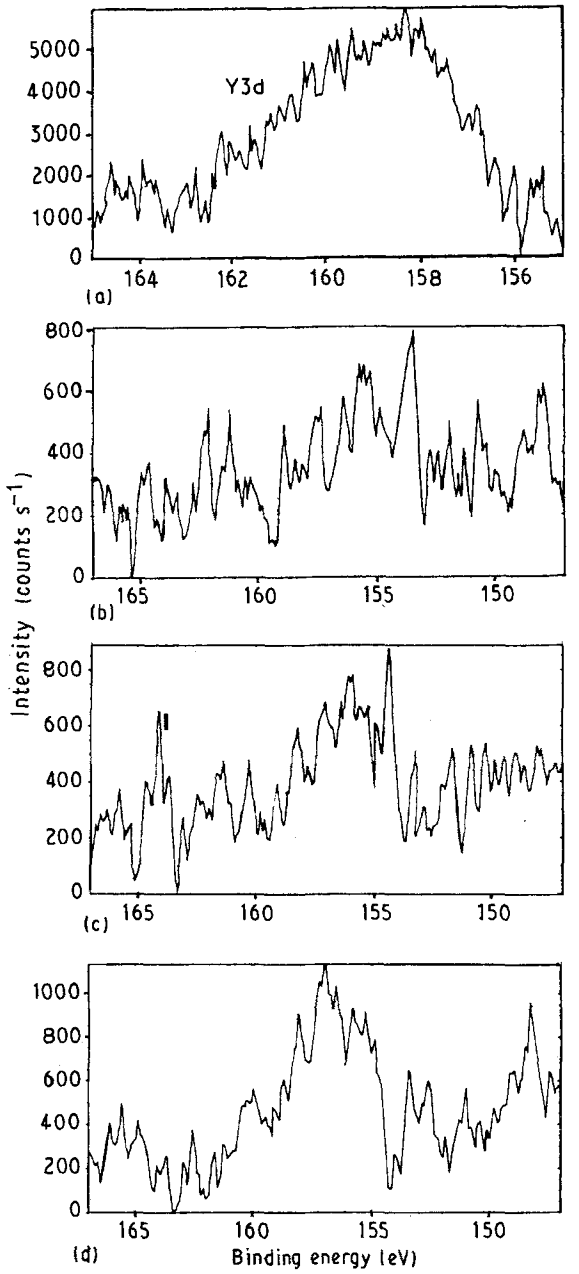


Figure 4 XPS traces for ZTA as a function of ageing in 20 vol % HCl, for Y 3D peaks. Note the initial drop in intensity of the Y peak after ageing for 3 months. Extended ageing produced no further change in intensity. (a) unaged; (b) 3; (c) 6; (d) 12 months.

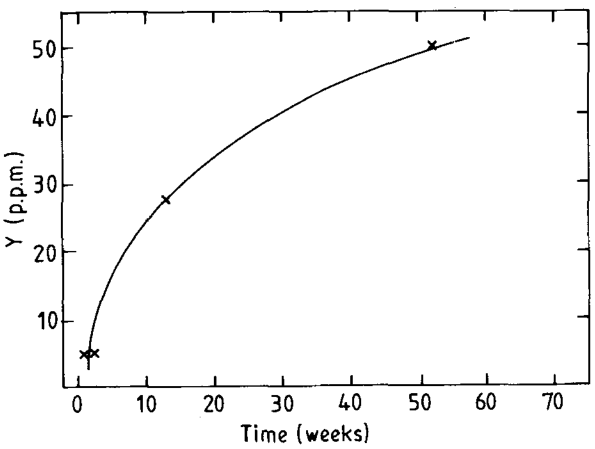


Figure 5 Y concentration of the ageing solution as determined by AAS, as a function of time of ageing for ZTA in 20 vol % HCl.

progressively more difficult for the remaining tetragonal particles to transform. Also, the more unstable larger particles will transform first, even at relatively high yttrium content, leaving the more stable smaller particles to transform later if their yttrium content is reduced sufficiently.

From the above discussion, one would expect the surface chemical analysis to show a decrease in the proportion of yttria after ageing in hydrochloric acid. However the results from the SIMS analysis were inconclusive. On the other hand, XPS data showed a slight decrease in yttrium content, but no change in zirconium content. In order to explain why there was no significant variation in the surface analysis data, one must assess the relative depletion of the yttrium from the ZTA. If the 50 p.p.m. yttrium (the amount detected in the 20 vol % HCl solution after 12 months) is related to the total amount of yttrium in the ZTA, i.e. 3 mol % of the 20 wt % ZrO_2, then 50 p.p.m. corresponds to $\simeq$ one twelfth of the total amount of yttrium in the ZTA. Thus changes in surface composition that we are trying to detect are around the limit of the resolution of the SIMS technique. There is also the added difficulty that even though the difference is one twelfth, the total amount of yttrium in ZTA is very small.

Two mechanisms have been proposed for the degradation in properties of TZP materials by ageing at elevated temperatures in humid and aqueous environments. The first, proposed by Sato and Shimada [2], is that the presence of water at the crack tip causes a reaction between the water and the Zr–O–Zr bonds, with the formation of Zr–O–H, leading to an increase in the pre-existing flaw size. Sato and Shimada [2] did not observe any weight change of the samples during ageing, and hence concluded that dissolution of yttria or zirconia into the solvents cannot play a major role in the strength degradation. The second mechanism involves the progressive leaching of yttrium from the surface tetragonal zirconia grains, leading to transformation to the monoclinic phase and associated microcracking. This was proposed by Lange *et al.* [3] who identified crystallites on the surface of thin foils as α-$Y(OH)_3$, an observation consistent with the leaching mechanism.

The two mechanisms proposed above were for TZP materials aged in the presence of water vapour or aqueous environments, at temperatures in the range 100–300 °C. In comparison, the present study concentrates on the effects of aqueous environments on the stability of ZTA under ambient conditions. From the experimental evidence, it is considered that the dissolution of yttrium from the solid solution is of prime importance. The ageing solutions which have been shown to lead to a degradation in properties and an increase in the percentage of monoclinic phase, have also exhibited the presence of dissolved yttrium. Sato and Shimada did not carry out any analysis of either the environment or the zirconia samples, and arrived at the conclusion that yttria was not leached out by determining the relative weight losses after ageing. It is suggested that this method of assessment may not possess the sensitivity necessary to detect such small variations in yttria content of the sample. A further point of contradiction is in the role of acid or base additions. No noticeable influence on the formation of monoclinic zirconia was determined by Sato and Shimada [2] by the addition of either acid or base constituents; however in the results presented here, it is evident that there was no increase in the monoclinic content after ageing in distilled water for 24 months, whereas the addition of 1% HCl had a significant effect on the monoclinic transformation and therefore on mechanical properties. An explanation of these apparent differences comes from the relative temperatures of the two ageing studies. Sato and Shimada [2] have shown that at 100–200 °C the reaction kinetics favour water as the corrosive medium, such that the effects of acid additions in this temperature range are swamped. Thus one can only detect the effect of HCl if the water is ineffective, and this appears to be the case at ambient temperature. It can be shown using the activation energies of Sato and Shimada [2] that to achieve the maximum monoclinic content at 20 °C ageing times must be in excess of 39 years; similarly to achieve only 20% transformation, the ageing times needed are in excess of 2 years. Comparing the predicted ageing times for room-temperature ageing in water, with the experimental observations of 1.5 mm penetration and 58% monoclinic zirconia after 6 months in HCl, it is evident that this level of attack cannot occur by the same mechanism as that for water at elevated temperatures. It is therefore concluded that the corrosion mechanism present in the room temperature ageing of ZTA in HCl is not the same as occurs when zirconia is aged at 100–200 °C in water.

On the other hand, the transformation to the monoclinic phase which occurs in the ethylene glycol solution at 80 °C after many weeks of ageing may be the same as reported in zirconia at elevated temperatures in water as, unlike in HCl solutions at room temperature, no yttria was detected in the ethylene glycol solution after ageing at 80 °C. However, using the activation energy derived by Sato and Shimada [2], it was calculated that at 80 °C the maximum amount of monoclinic zirconia would occur after ageing for around 70–130 days, well within the time schedule of the present study. In the present work, the monoclinic content only reached 32.5% after ageing for 2 years. This would tend to suggest that either (i) a different corrosion mechanism was operating for ZTA with a different activation energy, compared to that previously reported for zirconia at these temperatures; or (ii) the presence of ethylene glycol reduced the effectiveness of water in promoting the transformation to monoclinic.

However, (i) is unlikely, as work by the authors on zirconia and ZTA aged in Ringer's solution at 37 °C, suggests that the process was the same for both materials as for zirconia in water [5]. This supports the view that the ethylene glycol served to inhibit the t → m transformation.

The mechanism proposed by Lange *et al.* [3] realises the importance of yttrium dissolution, and the observations made are in agreement with the phenomenological evidence of the present study with HCl solutions. It is likely that the process of degradation observed in the present work in HCl solutions is similar to that described by Lange *et al.*, namely that the yttrium is leached from the zirconia-based solid solution in the form of a hydroxide, which is more stable under hydrothermal conditions than Y_2O_3. The decreased stabilization leads to the transformation of the zirconia to the monoclinic polymorph, and is associated with microcracking of the matrix.

One further point is the role of the alumina matrix in the degradation process: the earlier studies have examined only zirconia materials. It has been shown [7] that the alumina matrix material suffers a small loss in strength and fracture toughness on ageing. If the matrix suffers a degradation in strength, it is likely that the constraint imposed on the zirconia particles by the matrix will be reduced. This in turn would lead to transformation of the less stable zirconia particles (i.e. larger sized particles), and hence an increase in the monoclinic content. In Part II of this study [7] the close relationship between the transformation to the monoclinic phase and the degradation of mechanical performance will be established. The strengths of ZTA and alumina D995A (normalized to the unaged values) are presented in Fig. 6 as a function of ageing time in 20 vol % HCl. It can be seen that both materials exhibit an initial rapid decrease in strength over a period of about 1 week, but the strength of ZTA continues to fall whereas that of D995A remains approximately constant. This indicates that changes in the alumina matrix are only likely to play a role in promoting the tetragonal to monoclinic transformation in the first weeks of ageing, and do not influence the behaviour of the ZTA particles over longer periods.

The importance of the stabilizing oxide has been described above, and the consequence of its removal on the mechanical properties has been demonstrated. If the stabilizing oxide were changed so that it was no longer leached by the HCl, the decline in properties would be less severe. A preliminary investigation [9] into the effect of hydrochloric acid on the t → m transformation of ceria-stabilized TZP showed that

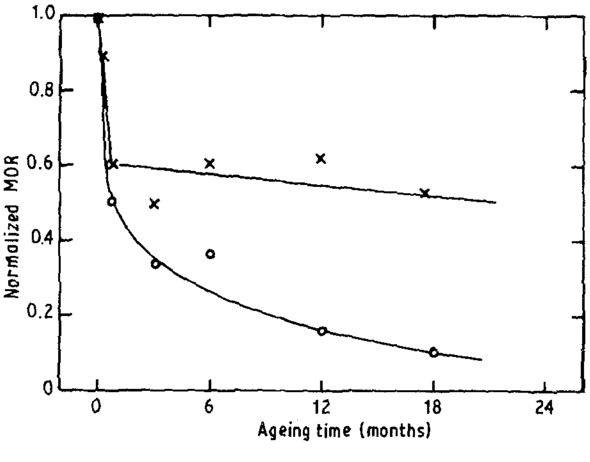


Figure 6 Normalized MOR of (○) ZTA and (×) D995 aged in HCl. ZTA exhibited a greater decrease in relative strength compared to D995; whereas D995A reached a limiting strength, ZTA continued to degrade with increasing ageing time.

the percentage of monoclinic zirconia remained unchanged after ageing for 26 weeks. Furthermore, it has been reported that doping the surface of Y–TZP with ceria improves the thermal stability in humid atmospheres [4]. In light of these findings and the present results, it appears that the stability of zirconia materials in certain aqueous solutions may be improved either by surface doping with ceria, or by using ceria as the stabilizing oxide.

5. Conclusions

1. Of the liquid environments studied, only HCl solutions produced a significant increase in the monoclinic content of ZTA on ageing at room temperature. Ageing in ethylene glycol solution at 80 °C also induced some particles to undergo the tetragonal to monoclinic transformation.

2. Examination of the behaviour of ZTA in HCl solutions revealed an increase in the proportion of monoclinic zirconia at the surface with increasing ageing time. Dye-penetrant and microscopy showed that the acid had been able to permeate the body of the ceramic through a network of microcracks, which after prolonged ageing linked to form macrocracks. Analysis of the ageing solutions indicated an increase in yttrium content, which must have been leached from the zirconia–yttria solid solution with time. However, surface analysis by XPS and SIMS did not provide conclusive evidence of a depletion of yttrium at the surface; this is probably because the relative proportion of yttrium removed during the leaching process was only of the order of one twelfth of the total amount of yttria in the original ZTA, and this approaches the limit of detection of the technique.

3. The proposed mechanism of attack in HCl solutions at ambient temperature is that the yttrium is leached from the surface, reducing the stability of the tetragonal zirconia and hence promoting the diffusionless transformation to the monoclinic structure. Associated with the transformation is the formation of microcracks, which provide a free path for the acid to attack virgin surfaces within the ceramic.

4. The effect of the concentration of HCl on the depth of attack, monoclinic ratio and yttrium content of the ageing solution was not significant at long ageing times. However, after short ageing times (less than 3 months) there was an increase in both the depth of attack and the yttrium content with increasing concentration.

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