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Chemical stability of yttria doped zirconia membranes in acid and basic aqueous solutions: chemical properties, effect of annealing and ageing time

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Abstract

Corrosion resistance of 3Y–ZrO_2 microfiltration membrane was evaluated at room temperature and 80°C in aqueous solutions of acids and bases. Chemical properties were investigated in order to explain the chemical attack and the effect of elemental dissolution on the phase transformation. Dissolution of yttria was detected in acid solutions of low pH except in HF solution. In the basic solutions, dissolution of Y and Zr was negligible. Silica dissolved both in acid and basic solutions. As a result of chemical reactions and dissolution of ions, pH after corrosion showed a shift to higher values in acid solutions and to lower values in basic solutions, indicating the amphoteric reactions in 3Y–ZrO_2. Samples corroded in acid and basic solutions at 80°C were annealed at 1200°C after the corrosion test. Phase transformation was completely reversible in the samples tested in basic solutions. The sample in acid solution showed partial re-transformation of the monoclinic phase due to the dissolution of yttria. The effect of corrosion time was studied for aqueous solutions of HF and HCl. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: C. Corrosion; E. Membranes; 3Y–ZrO_2; Stability; Dissolution; Annealing

1. Introduction

Yttria-doped zirconia polycrystals Y-TZP are well known among oxide ceramics for high strength and high fracture toughness that makes them suitable for many applications [1,2]. Thermal stability and high corrosion resistance of Y-TZP membranes are currently attracting considerable interest in high-temperature (200–1000°C) applications and harsh chemical media [3–5]. These properties make porous 3Y–ZrO_2 ceramic a good candidate for membrane applications. It is interesting to see whether porous 3Y–ZrO_2 exhibits the same properties as dense counterpart in lower extent, limited by the level of porosity. However, one of the drawbacks of Y-TZP ceramics is their low-temperature degradation in humid media; there is a decrease in mechanical properties with ageing at low to medium temperature service (65–500°C) that restricts the industrial applications [6]. Degradation involves the transformation of the tetragonal phase to monoclinic, which results in a volume change during phase transformation that creates micro- and macro-cracks and degrades the mechanical properties drastically. Hydrothermal degradation is more severe in water and at elevated pressures above 100°C [7]. To maintain good mechanical properties it is important to retain the tetragonal structure in service.

The hydrothermal degradation of dense yttria-doped tetragonal zirconia polycrystals has been investigated and discussed previously [8–15], but not in detail in porous structures. Sato et al. [16] have studied the corrosion behaviour of 3Y–ZrO_2 dense ceramic in different aqueous solutions of acids and also in nonaqueous solutions. Although there is not yet a consensus on the mechanism of degradation [12], it is evident that the degradation is a surface dependent phenomenon and proceeds from the open surface to the interior of a component. Therefore, porous Y-TZP, e.g. membranes, having a higher surface area than the dense counterpart due to open porosity, are expected to show more severe damage due to degradation. Many applications of Y-TZP microfiltration membranes in the treatment of wastewater [17], in the chemical [18] food and beverage [19], as well as the pulp and paper industries [20],

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involve aqueous media and chemicals that contain active ions. The change of properties of porous Y-TZP under hydrothermal and corrosive attack is thus important from a practical point of view in such applications and needs to be studied properly.

The aim of this study was to find out the combined effect of aqueous solution and corrosive ions, in acidic and basic media, on porous 3Y–ZrO_2 and the relation between hydrothermal attack and chemical or corrosive attack. Structural properties after the corrosion test such as weight change, phase transformation, porosity, hardness and microstructure have been reported in another paper. In this study, changes of chemical properties, elemental dissolution, reversibility of phase transformation after annealing and the effect of ageing time are reported. It must be noted that in this paper, hydrothermal attack is referred to the effect of water on 3Y–ZrO_2 solely, excluding the effect of ions in acid or basic solutions and corrosive attack is referred to the effect of corrosive ions other than OH^- in solutions of acids and bases (although hydrothermal attack can involve also corrosion attack).

2. Materials and methods

Microfiltration membranes were prepared by slip casting from 3Y–ZrO_2 powder HSY3 supplied by Zirconia Sales (UK). HSY3 powder contained 93 wt.% ZrO_2 and HfO_2, 5.25 wt.% Y_2O_3, and the main impurities in wt.% were 0.295 Al_2O_3, 0.315 SiO_2, 0.058 TiO_2, 0.01 CaO, 0.039 Fe_2O_3 and 0.01 Na_2O. Particle size was monomodal centered at 0.5 μm and the specific surface area was 7 m^2/g measured using the BET method. The crystallite size of the polycrystalline powder was 100 nm. The phase composition was measured by X-ray diffraction XRD (D500 Diffractometer, Siemens) using Cu–K_α radiation. The volume fraction of the monoclinic phase was determined from XRD data, using the Nickolson–Garvie equation [21]. The microstructure of samples was characterized by analytical electron microscopy SEM (XL 30, Philips) equipped with an energy dispersive X-ray analyser (EDAX, Philips). Membranes sintered at 1200°C for 3 h with a 5°C/min heating and cooling rate, had a narrow pore size distribution centered at 100 nm, containing around 24% porosity and having a specific surface area of 2.4 m^2/g and a 100% tetragonal phase structure. Microhardness of unsupported membranes sintered at 1200°C for 3 h was 220 ± 20 $HV_{0.3}$.

Corrosion tests were carried out on unsupported membranes at room temperature for 79 days and at 80°C for 34 days in a closed, static system. Properties were measured at room temperature. Samples of unsupported membranes were cleaned in an ultrasonic, deionized water bath, before loading in the corrosion cell (200 ml polymer can). The pHs of solutions after the corrosion test were detected at room temperature. The corroded solutions after the tests were analyzed by inductively coupled plasma emission spectroscopy (ICP–ES) (Perkin Elemer ICP 2000). The effect of the corrosion time was studied on samples tested in HF and HCl solutions for the given period of time in separate cells. The Vickers hardness (HV) was measured (Shimadzu Microhardness Tester) using 300 g load for 15 s at maximum load. The reported values are the averages of ten measurements.

3. Results and discussion

3.1. Dissolutions into the solutions

Dissolution of Y, Zr and Si ions was measured in highly acidic and basic solutions after the corrosion test at room temperature (RT) and at 80°C. The results are shown for the RT test in Table 1 and for 80°C in Table 2, together with the measured amount of m-phase of the samples. Dissolution of yttrium is of major concern since yttria is the stabilizing agent in Y-TZP ceramics. The dissolution of yttrium was high in acid solutions

Table 1
Dissolution rate of Y, Zr and Si in acid and basic solutions and amount of m-phase in the samples after corrosion test at RT for 79 days[a]

	Dissolution rate of ions (ppm/day/g)×10^{-3}			
Solution (pH)	Y	Zr	Si	m-phase (%)
H_2SO_4 (2)	26	< 1	15	< 1
HNO_3 (2)	27	< 1	13	2
HCl (2)	23	0	11	< 1
HF (3)	< 1	< 1	8	1
NaOH (12)	< 1	< 1	16	3
NH_4OH (11.5)	0	0	6	3

[a] Results are normalised per g of sample weight.

Table 2
Dissolution rate of Y, Zr and Si in acid and basic solutions and amount of m-phase in the samples after corrosion test at 80°C for 34 days[a]

	Dissolution rate of ions (ppm/day/g)×10^{-3}			
Solution (pH)	Y	Zr	Si	m-phase (%)
H_2SO_4 (2)	101	< 1	59	4
HNO_3 (2)	96	< 1	33	9
HCl (2)	85	0	33	3
HF (3)	< 1	< 1	47	4
Distilled water	0	< 1	10	0
NaOH (12)	0	0	26	< 2
NH_4OH (11.5)	0	0	15	9

[a] Results are normalised per g of sample weight.

(pH 2) of HNO_3, H_2SO_4 and HCl at both temperatures. Lower dissolution of yttrium was found in HF solution at pH 3 both at RT and 80°C. The dissolution of elements is controlled by chemical reactions and by the diffusion of ions through the product layer [22]. The low dissolution of yttrium in the HF solution is attributed to the formation of insoluble YF_3 according to the following reaction [23] that protects surface from further dissolution:

$$Y_2O_3 + 6HF \Longleftrightarrow 2YF_3 + 3H_2O$$

Shimada and Sato [22] showed that, in silicon nitride ceramics, Si and Al ions were dissolved in HF solutions but Y was not dissolved. Lange et al. [15] also showed that in the presence of acids and neutral solutions, yttrium dissolves in the form of Y^{3+} ions. We found the dissolution of yttrium negligible in basic solutions of NaOH and NH_4OH as well as in water at RT and 80°C. This was expected since yttrium is almost insoluble in bases [24]. In the presence of alkaline solutions, and also in aqueous solutions of pH 6.5–8.5, yttria tends to convert, by spontaneous hydration, to hydroxide $Y(OH)_3$ that is the stable equilibrium form [23,25]. Dissolution of yttrium is influenced by the specific surface area and sintering temperature. The lower the specific surface area and the higher the sintering temperature, the lower is the amount of yttrium dissolved [14]. Dissolution of yttrium from HSY3 membrane has been found to be lower than the yttrium dissolution from HSY3 powder in HNO_3 solution at pH 2 [26]. This is attributed to the lower surface area of the membrane and the effect of sintering, which stabilizes yttria against dissolution. In 3Y–ZrO_2 membranes the dissolution of yttrium is enhanced as compared to dense components, due to the higher surface area exposed to the media and the lower sintering temperature applied in the processing of membranes.

Depletion of yttrium leads to the transformation of the metastable tetragonal zirconia to monoclinic. Hydrothermal attack in a water solution without acids or bases also results in phase transformation. Dissolution of yttrium was high in HNO_3 solution and negligible in NH_4OH at 80°C. However, the amount of m-phase in both samples was around 9%. From these results, it is suggested that in acid solutions the depletion of yttria and hydrothermal attack by OH^- ions to the lattice resulted in phase transformation. In basic solutions, depletion of stabilising agent, however, does not play a role and hydrothermal attack was the dominant mechanism that caused phase transformation.

Dissolution of zirconia was negligible in all solutions at RT and 80°C. At 80°C the dissolution of Y and Si was higher. Dissolution of Si was found in both acid and basic solutions. Although Si is one of the minor elements in the composition of 3Y–ZrO_2, since it usually segregates to the grain boundaries, its dissolution is

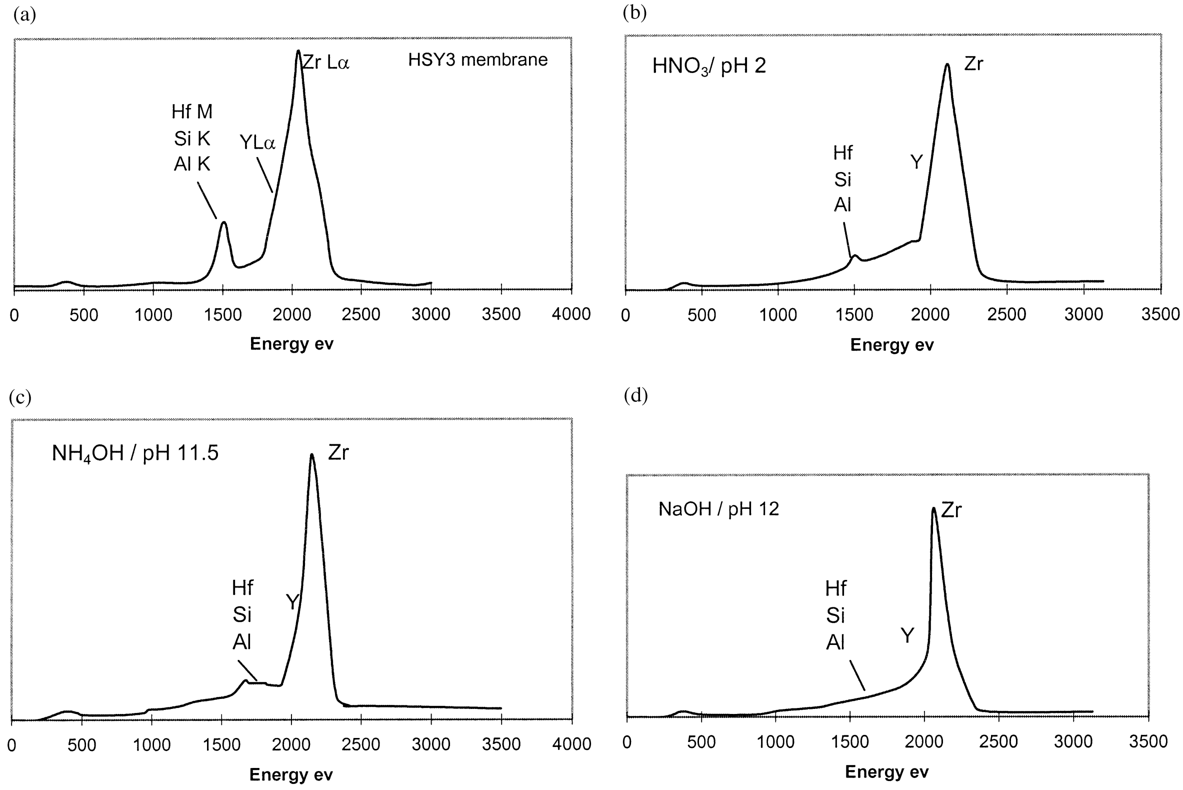

Fig. 1. EDS spectra of HSY3 sintered membrane (a), and samples tested in (b) HNO_3 at pH 2 (c) NH_4OH at pH 11.5 and (d) NaOH at pH 12 at RT for 79 days.

important in porous structure when the properties of grain boundaries are concerned.

3.2. EDS studies

Chemical composition of some of the samples after the corrosion test at RT was studied by EDS (Fig. 1). Si and Al K-peaks and Hf L-peak appear almost in the same level of energy. Some of the samples tested at RT were studied by EDS at a low energy range without a thin gold coating. It is difficult to distinguish Y and Zr L-peaks, since the Y peak lies in a slightly lower energy level than the Zr peak and can be buried in the Zr peak, especially when the amount of Y is much less than that of Zr.

In EDS spectra of samples tested in HNO_3 and NH_4OH the overlapping peaks of Si, Al or Hf were smaller compared to the peak in the sintered membrane. The Si peak was removed in the spectra of samples in NaOH and NH_4OH solutions, which was in agreement with the dissolution of Si (Table 1). It indicates the dissolution of Si in both samples, which was also detected in solution analysis. It was not possible to detect whether the Si peak was from the compounds in grain boundaries or grain interiors due to the low resolution in SEM. K-peaks of Y and Zr at higher level of energy (14–16 kev), in which peaks were separated and distinguishable, did not show any difference between the unexposed and corroded samples.

3.3. pH of solutions after corrosion tests

The change of pH after the corrosion test at RT and 80°C is presented in Figs. 2 and 3. The ionic exchange between the corrosive media and zirconia membrane surface in chemical reactions or dissolution results in a change of the pH of solutions. This indicates the extent of reactions, which involve H^+ and OH^-, between the solutions and the membrane. The distance of points from the diagonal line shows the deviation of pH in solutions after the corrosion test from the initial pH of the solutions. Considering the logarithmic nature of pH, it is obvious that a small shift in low acidic pH or high basic pH values indicates a high number of ionic exchanges, and as the pH shifts toward neutral from both sides, the change in pH is higher with the same number of ionic exchanges.

Zirconia is amphoteric in nature, which means that different reactions are dominant in acid and basic solutions. These reactions can be modelled by the following acid–base reactions:

$$MOH + H^+ \leftrightarrow MOH_2^+$$

$$MOH + OH^- \leftrightarrow MO^- + H_2O$$

where the proton is, in fact, the potential determining ion. The net surface charge of HSY3 membrane at each given pH, depends on the surface potential of the membrane that in this case can be assumed to be about the same as that of the powder used to produce the membrane. The isoelectric point (iep) of HSY3 is 7.6, which means that at this pH the net surface charge is zero, or the positive and negative charges are equal [26]. Below the pH of iep, the net surface charge is positive and above that it is negative. Due to the amphoteric nature of the zirconia surface, different types of chemical reactions at each given pH are favoured, depending

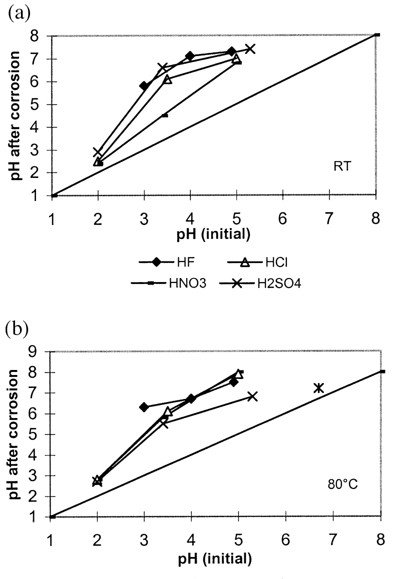

Fig. 2. PH of solution after corrosion of HSY3 samples in acid solutions (a) at RT for 79 days and (b) at 80°C for 34 days.

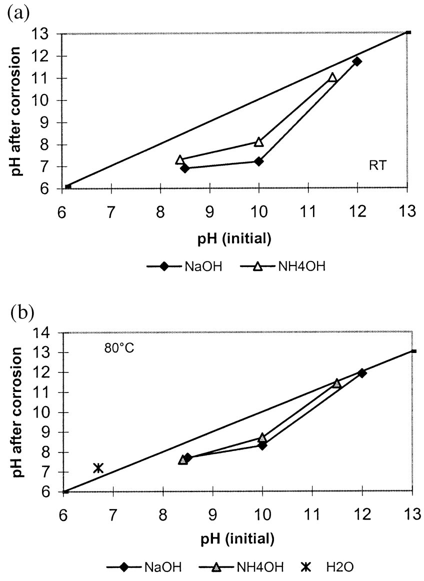

Fig. 3. PH of solution after corrosion of HSY3 samples in basic solutions (a) at RT for 79 days and (b) at 80°C for 34 days.

on the net surface charge of the membrane and ions in the solution. When the concentration of the potential determining ion is altered, the relative adsorption of ions on the surface varies [27].

In acid solutions, and below the iep of the membrane, the pH after corrosion shifted to higher pH values and in basic solutions and above the pH of iep, to the lower pH values, due to the amphoteric reactions of zirconia. In both acid and basic solutions, the shift of pH in solutions after corrosion was higher in the middle pH point (pH 3.5–4 in acid solutions and pH 10 in basic solutions) at RT and 80°C. Rosenholm et al. [28] also reported that for 3Y–ZrO_2 powder, the peak in the pH change was at pH 4 in the acid range of pH below the iep of powder and in basic pH, the maximum change was found at pH 9, above the iep.

It is speculated that at highly acidic and basic pH, i.e. pH 2–3 and 11–12 respectively, the ionic density is high and the ionic exchange between the corrosive solutions and the membrane surface is controlled by kinetics of corrosion. At slightly acidic and basic pH (pH ~5 and 8.5) the corrosive reactions are limited by the number of reactive ions in the solutions and it justifies the lower pH change at this range of pH. The higher shift of pH in acid and basic solutions at pH 3–4 and pH 10, is attributed to the enhancement of chemical reactions due to a positive balance between the number and the density of active ions.

3.4. Thermodynamic and kinetic aspects of hydrothermal corrosion

The degree of attack in corrosive media depends partly on the thermodynamic properties of reactants and products, but can also be greatly influenced by kinetic effects. A layer of protective product can limit the corrosive attack. The corrosion product could be dense and protective or porous and non-protective. The production of thin protective layers of $ZrSiO_4$ and YF_3 that hinder the corrosion process are examples of such products in Y–ZrO_2. When assessing the likelihood of the reduction of an oxide ceramic, a comparison of the free energies of formation of the reactants and likely reaction products, at the temperature of interest, will indicate whether or not there is a driving force for the reaction. If there is, the extent of reaction may nonetheless be restricted by poor wetting or limited by a layer of reaction products. All thermodynamic calculations are valid for equilibrium systems whereas many ceramic systems never reach equilibrium. Ideally, equilibrium studies should be completed by kinetic experiments in order to build a more complete picture of the interactions. Despite the limitations of thermodynamic studies, it can often save a great deal of unnecessary experimental work by indicating which types of material are unlikely to be corroded.

In aqueous solutions, hydration of zirconia may take place to form zirconium hydroxides: $ZrO_2.H_2O$ and $ZrO_2.2H_2O$. The solubility of zirconium hydroxide is much lower than zirconia [23]. The chemical properties of zirconia also depend on the method used to prepare it. If it is strongly calcined, it is practically insoluble in all acids. Zirconium shows itself to be a very base metal, dissolves as zirconic ions Zr^{4+} and zirconyl ions ZrO^{2+} in highly acid solutions and as zirconate ions $HZrO^{3-}$ in very alkaline solutions [23]. In our experiment, dissolution of zirconium was negligible in the range of pH in acid and basic solutions.

Silica is dissolved as silicate SiO_3^{2-} almost simultaneously in very alkaline solutions (NaOH, KOH) [23]. Dissolution of Si is also high in HF solutions. The affinity of chemical reaction of the corrosive ions with the surface or grain boundaries is important to define the corrosion rate. Since most of the Si compounds appear in the grain boundaries, the dissolution of Si is important to the chemistry and strength of the grain boundaries. The effect of grain boundary chemistry and the possible reactions of the ions in corrosive media with grain boundaries are more important in acid and basic corrosion processes than in hydrothermal attack in water or humid media. In practice, dissolution of Si occurs in all these solutions, even neutral solutions to a different extent, as our results showed. The amount of dissolution depends on not only the pH of the solution, but also on the ionic strength of the solution, the species in the solution and the Si-compound. Re-precipitation of Si on the surface after a period of time is also possible. Dissolution of Si was considerable in our case both in the basic and acidic solutions. Part of the Si dissolved in the solutions may derive from the aluminosilicate grinding balls that were used in milling of the slip.

Diffusion of ions through the double layer and removal of corrosion products from the surface could be the controlling step of the reaction and inhibit the corrosion process. In solutions of high ionic density the double layer is thin but crowded (compact) and ions have difficulty in passing through the double layer to react at the surface. This condition is met in our experiment in highly acidic pHs of 2–3 and highly basic solutions of pH 11–12. Shimada [22] showed that the dissolution of ions was less in 10 M solutions of HF and HCl than in 0.1 M solutions due to the high ionic density inside the double layer.

3.5. Annealing after corrosion tests

Samples that were tested at 80°C in HNO_3 and HF solutions and in NaOH and NH_4OH solutions at highly basic pH were annealed after corrosion at 1200°C for 3 h with a 5°C/min heating and cooling rate (the same schedule used in the sintering of unexposed samples). After annealing the phase composition and microhardness

Table 3
Phase composition and microhardness after corrosion test at 80°C, and after annealing at 1200°C for 3 h[a]

Corrosive media (pH)	HNO_3 (2)	HF (3)	NaOH (12)	NH_4OH (11.5)
m-phase after corrosion (%)	9	4	<2	9
m-phase after annealing (%)	5	2	0	0
Concentration of Y in solution (ppm/day/g)$\times 10^{-3}$	96	<1	0	0
Hardness after corrosion (HV)	247	280	240	247
Hardness after annealing (HV)	268	293	269	310

[a] Hardness of sintered membrane was 220 HV after sintering at 1200°C for 3 h.

were measured and are shown in Table 3. In basic solutions, the monoclinic phase was totally re-transformed to tetragonal after annealing in the samples. The amount of m-phase in the samples tested in HNO_3 and HF reduced after annealing, but did not reach to zero.

Sato and Shimada [16] proposed the mechanism of phase transformation and degradation which is based on the diffusion of OH^- into the lattice in the oxygen vacancies. In this mechanism the depletion of yttria plays no role in inducing phase transformation, since no dissolved yttria was found in the aqueous solutions. The diffusion and migration of OH^- into the lattice accompanies a lattice expansion. Phase transformation is reversible by annealing and the initial lattice parameters could be restored by the exclusion of OH^-. Nakajima et al. [29] also showed that in basic solutions dissolution of yttrium did not play an important role and hydrothermal attack was dominant and responsible for phase transformation.

Reversible phase transformation and lack of yttria dissolution in the samples in basic solutions suggested the mechanism of hydrothermal attack based on diffusion of OH^- into the lattice. In HNO_3 solutions yttria was dissolved and phase transformation was not totally reversible due to the depletion of stabilising agent. The tetragonal phase restored to a level depending on the amount of yttria remaining in the sample after the corrosion test. In HF solution, although the dissolution of yttria was negligible, yttria was depleted by formation of solid YF_3, therefore the level of yttria after corrosion was lower and tetragonal phase could not be restored totally.

It is suggested that in basic solutions, mechanisms of hydrothermal attack by OH^- on the lattice were the dominant mechanisms and in acid solutions, in which yttria dissolution occurred both mechanisms of hydrothermal attack by OH^- to the lattice and yttria depletion have induced phase transformation. However, as the results of corrosion in acid and basic solutions showed, the dissolution of yttrium and chemical reactions in the samples in acid solutions did not enhance the phase transformation induced by hydrothermal corrosion. Govila [30] reported the same phenomenon in the annealed dense samples.

Grain boundaries are particularly prone to chemical changes due to the chemical attack of corrosive ions in acid and basic solutions to the minor impurities segregated in grain boundaries. Hydrothermal attack by OH^- is most likely proceeding by diffusion into the lattice. This suggests that the differences in the grain boundary composition and the processing route of the powder and membrane play an important role in defining hydrothermal corrosion resistance.

The increase in hardness of samples after annealing is mainly attributed to extended sintering time (3 h sintered and 3 h annealed) at 1200°C, as well as the lower porosity of the annealed samples and lack of micro-cracks in the samples after phase transformation.

3.6. *Effect of time on hydrothermal corrosion at 80°C*

The effect of corrosion time was studied in the samples in acid solutions of HF and HCl at 80°C. Weight loss of the sample in HF solution at pH 3 increased as the exposure time increased to 600 h. A further increase of exposure time did not yield higher weight loss (Fig. 4). This can be attributed partly to the formation of insoluble YF_3 on the surface. The samples in HCl solution showed a steady increase in weight loss as a function of corrosion time.

Phase transformation of the samples in HF and HCl solutions showed the same trend; an increase and then a decrease as a function of the exposure time (Fig. 5). After about 300 h exposure the amount of m-phase reached a peak in samples in HCl solution and with the increase in ageing time up to 600 and 800 h the amount of m-phase diminished. The sample in HF solution

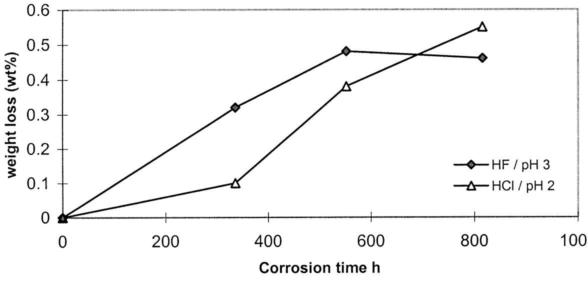

Fig. 4. Weight loss of samples in HF and HCl solutions at 80°C.

showed low m-phase up to 300 h, then it increased and after 600 h decreased to less than 2% after 800 h in solution. This behaviour cannot be attributed only to the dissolution of yttria in the solutions. Yttria dissolution was low in HF solution of pH 3 and high in HCl solution of pH 2 (Table 1).

Re-adsorption of dissolved yttria from the solution is possible but it could not lead to partial transformation of the m-phase to t-phase at 80°C. Thompson and Rawlings [31] also reported that both the rate of phase transformation and the dissolution of yttria decreased with increase in the exposure time in zirconia-toughened alumina in HCl solution.

Phase transformation and degradation occur over a range of temperatures in Y-TZP ceramics with a minimum and maximum limit that is defined by thermodynamic and kinetic facts. Above and below this temperature range, no phase transformation occurs and in this range of temperature the monoclinic phase shows a Gaussian distribution as a function of temperature. These temperatures depend on the amount of stabilizer (yttria) and the sintering temperature. Sato et al. [32] showed that for dense 3Y–ZrO_2 the lower limit of temperature was at 50–100°C in air and the upper limit increased from 250 to 400°C as the sintering temperature increased from 1450 to 1600°C. They also showed that the maximum amount of transformed monoclinic phase decreased from 80 to 10% as the sintering temperature of samples decreased. The lower amount of the monoclinic phase and the smaller range of temperature for phase transformation in the samples sintered at lower temperatures is due to the smaller grain size. HSY3 membrane was sintered at 1200°C and due to the fine grain size (0.1 μm; lower than the critical grain size for phase transformation) and limited grain growth at this temperature, phase transformation was not more than 10% in these samples.

Hydration of the surface is necessary for the adsorption and penetration of OH^- ions into the lattice vacancies. Dehydration of the surface is expected to inhibit this process. Dehydration of the particle surface has been reported based on electrophoretic mobility measurements in 3Y–ZrO_2 powder aged in water for 240 h [33,34]. Re-precipitation of Si and Y from the solution also might hinder the hydration of the surface.

It is possible that some monoclinic particles have broken off the surface due to the corrosion and phase transformation stresses in the samples exposed for 800 h and resulted in low monoclinic contents detected in these samples.

XRD spectra of samples corroded in HF and HCl solutions for different times are shown in Fig. 6.

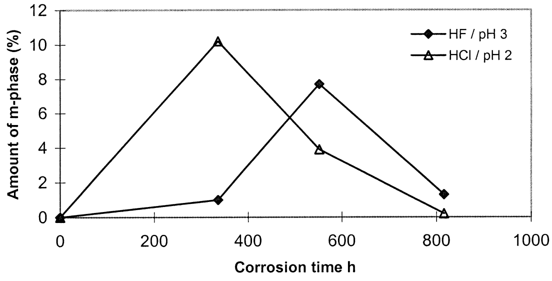

Fig. 5. The amount of m-phase in samples corroded in HF and HCl solutions at 80°C.

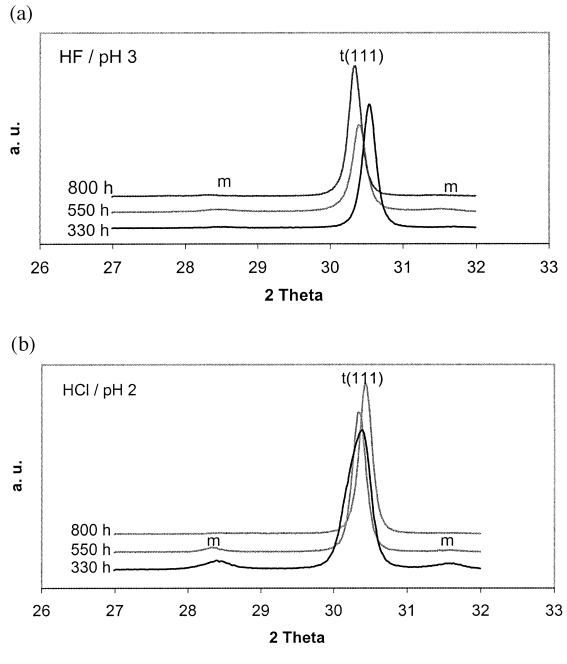

Fig. 6. XRD spectra of samples corroded in HF and HCl solutions at 80°C.

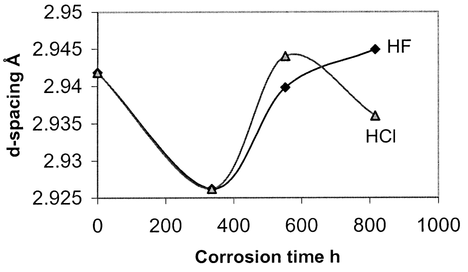

Fig. 7. Changes in lattice spacing of the samples in HF and HCl solutions at 80°C.

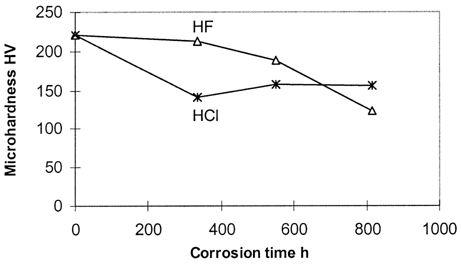

Fig. 8. Microhardness of samples in HF and HCl solutions at 80°C.

Tetragonal (111) peak of the sample in HF solution showed a shift to lower 2θ values as the exposure time increased. It indicates an increase in lattice spacing of the tetragonal phase as the corrosion time increases. Peak broadening can be seen in the tetragonal peak of the sample in HCl solution that showed the highest monoclinic phase after 330 h corrosion test. A small shift to higher 2θ values was seen in the sample in HCl as the ageing time increased, indicating a decrease in lattice spacing.

Lattice spacing was detected in both samples as a function of exposure time (Fig. 7). It must be noted that the penetration of OH^- ions into the lattice creates a stressed zone and expands the lattice. The stressed zone creates nucleation points for phase transformation to the monoclinic phase. The mismatch in lattice parameters of the tetragonal and monoclinic phase results in a compressive stress and a decrease in lattice spacing in the tetragonal phase. Lattice spacing of the sample in HF and HCl solutions decreased and then increased to about the lattice spacing of an unexposed sample and did not change much up to 800 h in solution. The change in lattice spacing of the sample in HCl solution can be explained by the amount of m-phase in the sample, as the sample with the highest amount of m-phase showed the lowest lattice spacing.

The same trend in lattice spacing in samples in HF solution is not in agreement with the change in the amount of m-phase of the samples. There are other sources of stress in a hydrothermal corrosion test that affect the lattice spacing, such as stress due to the chemical adsorption of OH^- to the surface, chemical corrosion stress and anisotropy of thermal expansion and thermal expansion mismatch of the phases.

Microhardness of both samples decreased after corrosion (Fig. 8). The hardness of the sample in HF solution was higher than that of the sample in HCl solution up to 700 h. The sample in HCl solution reached the minimum hardness at 330 h exposure time, when the amount of m-phase reached a maximum of about 10% and then as the m-phase reduced with increase in exposure time, the hardness also slightly improved.

4. Conclusion

Dissolution of yttrium was found in acid solutions at RT and 80°C, the exception being in HF solutions which showed low dissolution of yttrium. Dissolution of zirconia was negligible in all the solutions and yttria did not dissolve in basic solutions and water. Si dissolution was detected in both acid and basic solutions. At 80°C, dissolution of Y and Si was higher. The pH of the solutions, after the hydrothermal corrosion test in acid solutions, showed a shift towards basic pH and in basic solutions a shift towards acidic pH, that emphasized the amphoteric behaviour of zirconia in these solutions. A higher shift of pH was found in the acid solutions of pH 3–4 and basic solutions at pH 10.

Annealing samples at 1200°C after the corrosion test at 80°C showed that samples in basic solutions totally restored the tetragonal phase, whereas the samples in acid solutions showed partial re-transformation of the monoclinic phase. It was suggested that in acid solutions dissolution of yttria and hydrothermal attack induced the phase transformation. In basic solutions, depletion of stabilizing agent plays no role and the mechanism of hydrothermal attack by OH^- ions to the lattice was dominant.

Weight loss of samples in HF solution increased with ageing time and then reached a plateau. Samples in HF and HCl solutions at 80°C showed an increase and then decrease in m-phase and an opposite change in lattice spacing was found. Microhardness of samples after the corrosion test showed a decrease.

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References

[1] R.C. Garvie, Stabilization of the tetragonal structure in zirconia microcrystals, J. Phys. Chem. 82 (1978) 218–224.

[2] T.K. Gupta, F.F. Lange, J. Bechtold, Effect of stress-induced phase transformation on the properties of polycrystalline zirconia containing metastable tetragonal phase, J. Mater. Sci. 13 (7) (1978) 1464–1471.

[3] K.W. Bird, K. Richardson, Zirconium for superior corrosion resistance, Ad. Mater. & Proc. 3 (1997) 19–20.

[4] P.D. Mercera, V.J.G. Ommen, E.B.M. Doesburg, A.J. Burgraaf, J.R.H. Roos, Stabilized tetragonal zirconium oxide as a support for catalysts: evolution of the texture and structure on calcination in static air, Appl. Catal. 78 (1) (1991) 79–96.

[5] A. Larbot, J.-P. Fabre, C. Guizard, L. Cot, New inorganic ultrafiltration membranes: titania and zirconia membranes, J. Am. Ceram. Soc. 72 (1989) 57–264.

[6] J.J. Swab, Low temperature degradation of Y-TZP materials, J. Mater. Sci. 26 (1991) 6706–6714.

[7] T. Sato, S. Ohtaki, T. Endo, M., in: P. Vincenzini (Ed.), High Tech Ceramics, Elsevier Science, Amsterdam, 1987, pp. 281.

[8] M. Hirano, Inhibition of low temperature degradation of tetragonal zirconia ceramics — A review, Br. Ceram. Trans. J. 91 (1992) 139–147.

[9] M. Yoshimura, T. Hiuga, S. Somiya, Dissolution and reaction of yttria-stabilized zirconia single crystals in hydrothermal solutions, J. Am. Ceram. Soc. 69 (7) (1986) 583–584.

[10] T.T. Lepistö, T.A. Mäntylä, A model for structural degradation of Y-TZP ceramics in humid atmosphere, Ceram. Eng. Proc. 10 (78) (1989) 658–667.

[11] J.F. Jue, J. Chen, A.V. Virkar, Low temperature aging of t′-zirconia: the role of microstructure on phase stability, J. Am. Ceram. Soc. 74 (8) (1991) 1811–1820.

[12] S. Lawson, Environmental degradation of zirconia ceramics, J. Eur. Ceram. Soc. 15 (1995) 485–502.

[13] T.T. Lepistö, T.A. Mäntylä, Degradation of TZP ceramics in humid atmospheres, in: D.E. Clark, B.K. Zoitos (Eds.), Corrosion of Glass, Ceramics and Ceramic Superconductors, Noyes Publications, Park Ridge, New Jersey, 1992, pp. 492–513.

[14] J.C. Farinas, R. Moreno, J. Requena, J.S. Moya, Acid–basic stability of Y-TZP ceramics, Mater. Sci. Eng. A109 (1989) 97–99.

[15] F.F. Lange, G.L. Dunlop, B.I. Davies, Degradation during aging of transformation-toughened ZrO_2–Y_2O_3 materials at 250°C, J. Am. Ceram. Soc. 69 (3) (1986) 237–240.

[16] T. Sato, M. Shimada, Transformation of yttria-doped tetragonal ZrO_2 polycrystals by annealing in water, J. Am. Ceram. Soc. 68 (6) (1985) 356–359.

[17] A.S.C. Chen, J.T. Flynn, R.G. Cook, A.L. Casaday, Removal of oil, grease, and suspended solids from produced water with ceramic crossflow microfiltration, Sep. Prod. Eng. (1991) 131–136

[18] J.M. Bauer, J. Elyassini, G. Moncorge, T. Nodari, T. Totino, New developments and applications of carbon membranes. Totino, Proceedings of the Second International Conference on Inorganic Membranes, France, 1991, pp. 207–212.

[19] T. Finnigan, R. Shackleton, P. Skudder, Using ceramic microfiltration for the filtration of beer and recovery of extract, Filtration Separation 26 (1989) 198–200.

[20] J. Nuortila-Jokinen, T. Uusluoto, M. Nyström, Removal of disturbing substances by ultrafiltration of make-up waters in the pulp and paper industry, Paper Timber 76 (1994) 256–261.

[21] H. Toraya, M. Yoshimura, S. Somiya, Calibration curve for quantitative analysis of the monoclinic-tetragonal ZrO_2 system by X-ray diffraction, J. Am. Ceram. Soc. 67 (1984) C–119.

[22] M. Shimada, T. Sato, Corrosion of silicon nitride ceramics in HF and HCl solutions, in: R.E. Tressler, M. McNallan (Eds.), Ceram. Trans. vol. 10, The Am. Ceram. Soc, Ohio, 1989, pp. 355.

[23] M. Pourbaix, Atlas of Electrochemical Equilibriuia in Aqueous Solutions (1974) 223–229 NACE Cebelcor.

[24] Handbook of Chemistry and Physics, 60th ed., CRC Press Inc., Boca Raton, FL, 1981, pp. B141.

[25] A.E. Martel, R.M. Smith, Critical stability constants, in: Inorganic Complexes, vol. 5 (1st Suppl.), Plenum Press, New York, 1982, pp. 105.

[26] F. Shojai, A.B.A. Pettersson, T. Mäntylä, J.B. Rosenholm, Electrostatic and electrosteric stabilisation of aqueous slips of 3Y–ZrO_2 powder, J. Eur. Ceram. Soc, 20 (3) (2000) 277–283.

[27] R. Moreno, The role of slip additives in tape casting technology: Part I — Solvents and dispersants, Am. Ceram. Soc. Bull. 71 (10) (1992) 1521–1557.

[28] J.B. Rosenholm, F. Manelius, H. Fagerholm, L. Grönroos, H.B. Fagerholm, Surface and bulk properties of yttrium stabilized ZrO_2 powders in dispersions, Prog. Colloid Polym. Chem. 97 (1994) 51–58.

[29] K. Nakajima, K. Kobayashi, Y. Murata, Phase stability of Y-TZP in aqueous solutions, Advances In Ceramics, vol. 12, Science and Technology of Zirconia, 1984, pp. 399.

[30] R.K. Govila, Strength characterization of yttria-partially stabilized zirconia, J. Mater. Sci. 30 (1995) 2656–2667.

[31] I. Thompson, R.D. Rawlings, Effects of liquid environments on zirconia-toughened alumina, J. Mater. Sci. 27 (1992) 2823–2830.

[32] T. Sato, S. Ohtaki, S. Endo, M. Shimada, Transformation of yttria partially stabilized zirconia by low temperature annealing in air, J. Mater. Sci. 20 (4) (1985) 1466–1470.

[33] M. Kagava, M. Omori, Y. Syono, Surface characterization of zirconia after reaction with water, J. Am. Ceram. Soc. 70 (9) (1987) 212–213.

[34] M. Kagava, Y. Syono, Y. Imamura, S. Usui, Surface characterization of ultrafine ZrO_2–SiO_2 powders by electrophoretic mobility measurements, J. Am. Ceram. Soc. 69 (3) (1986) 50–51.