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Structural stability of yttria doped zirconia membranes in acid and basic aqueous solutions

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Abstract

Hydrothermal corrosion behaviour of yttria doped zirconia (3Y–ZrO_2) microfiltration membranes was investigated in aqueous solutions of acids and bases at room temperature and 80°C in a static corrosion test. Unsupported membranes of 3Y–ZrO_2 prepared by slip casting had 100% tetragonal structure after sintering at 1200°C. Weight loss, phase composition, porosity, pore size and surface area as well as residual stress of the samples was measured after corrosion test. A weight loss was detected in all cases and it was higher at 80°C. There was no direct correlation between weight loss and the amount of monoclinic phase transformed from tetragonal phase. The results showed that in these solutions phase transformation of 3Y–ZrO_2 membrane occurred even at room temperature which is lower than the minimum range of temperature that has been reported for dense counterparts. However, the amount of monoclinic phase after corrosion was not more than 13% in the samples. Microcracks were not found in the samples with the highest amount of monoclinic phase after the corrosion test. Although phase transformation was found even at room temperature but the lack of microcracks prohibited the autocatalytic propagation of the phase transformation from the pore surface into the structure. 3Y–ZrO_2 membrane showed a good structural stability in these corrosive solutions despite having porous structure.

Keywords: Corrosion; Membranes; Phase transformation; Porosity; ZrO_2

1. Introduction

Ceramic membranes could outperform organic polymer membranes in numerous respects. Chemical stability under extreme pH conditions is one of the advantages of ceramic oxide membranes.[1] Porous zirconia is attracting increasing attention on account of its exceptional resistance to corrosion[2] in applications such as catalytic support or filtration.[3,4]

Tetragonal zirconia polycrystals (TZP) have excellent mechanical properties, which are associated with phase transformation strengthening and toughening due to tetragonal (t) to monoclinic (m) phase transformation. However, the drawback of Y_2O_3 stabilized tetragonal zirconia polycrystals (Y–TZP) is their hydrothermal degradation that refers to low temperature degradation of mechanical properties due to ageing in humid media at low temperatures, particularly in the water containing environments. This phenomenon was first reported by Kobayashi et al. in 1981.[5]

The degradation is caused by humidity or water induced phase transformation from tetragonal to monoclinic phase. The volume expansion associated to this phase transformation creates micro and macro cracks, which allow the humidity to penetrate into the structure, and creates propagation front from surface to the interior and degrades the mechanical properties. This can happen in temperature range from 65 to 500°C, with the maximum rate at 250°C.[6] This process is denoted hydrothermal degradation and it is described in details in recent reviews.[7,8]

Although the hydrothermal degradation of dense yttria doped zirconia ceramics has been investigated widely,[9–14] the phenomenon has not been studied properly in porous zirconia. High porosity and surface area are expected to enhance the degradation by hydrothermal attack, which is initiated from the surface. Porous ceramics and membranes are expected to show more severe damage by degradation because of the higher surface area and lower mechanical properties. The expansion of

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the applications of 3Y–TZP microfiltration membranes in harsh chemical environments and the use of chemical agents for cleaning need further detailed corrosion studies.

In this study, the hydrothermal corrosion behaviour of 3Y–TZP unsupported membranes was investigated in aqueous solutions of acids and bases. Hydrothermal corrosion in supported membranes with composite structure is complex in a dynamic flow through corrosion test and is influenced by a number of parameters besides the properties of the top layer material. Therefore hydrothermal corrosion test on unsupported membranes in a static condition was considered as a preliminary test to evaluate the changes in properties of 3Y–TZP top layer in which the flow condition and the interface corrosion in composite structure of supported membrane do not interfere with the results. Although to evaluate the performance of supported membrane, following dynamic test in close to service conditions is necessary and of industrial value.

In these solutions, the hydrothermal corrosion is combined with corrosive attack of ions in solutions. In this paper hydrothermal attack is referred to the effect of water and OH^- ions on the phase transformation and corrosion attack is referred to the chemical interaction of corrosive ions in acid and basic solutions with ceramic structure. Chemical reactions can also precede the hydrothermal attack. The variation in physical and structural properties of membranes such as weight loss, phase composition, porosity, pore size, and surface residual stress are reported.

2. Material and methods

Microfiltration membranes were prepared by slip casting from 3 mol% yttria doped zirconia HSY3 powder supplied by Zirconia Sales (UK). The chemical composition of powders was measured by X-ray fluorescence XRF (PW 1400, Philips). 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 and 0.01 Na_2O. Particle size was monomodal centred at 0.5 μm and specific surface area was 7 m^2/g measured by BET method using N_2 adsorption at the temperature of liquid nitrogen, −196°C (DeSorb/FlowSorb II 2300A, Micromeritics). The crystallite size of the polycrystalline powder was 100 nm. The phase composition was measured by X-ray diffraction technique using CuK_α radiation (D500 Diffractometer, Siemens). The volume fraction of monoclinic phase was determined from XRD data using the Nickolson–Garvie equation.[15] Microstructure was studied by scanning electron microscopy (SEM) (XL 30, Philips). Residual surface stress was measured by X-ray diffraction technique, using Cr-K_α radiation (Xstress 3000, Stresstech Oy).

Membranes sintered at 1200°C for 3 h had a narrow pore size distribution with the median size of about 120 nm, around 24% porosity and 2.4 m^2/g specific surface area. Unsupported membranes were used in all cases in corrosion tests and measurements. Corrosion tests were carried out at room temperature for 79 days and at 80°C for 34 days in a closed, static system. Samples were cleaned in ultrasonic deionised water bath before loading in corrosion cell (200 ml polymer can). Samples were boiled in deionised water for 2 h and remained in water for another 12 hour without heating. This arrangement is the same done in Archimedes' method for porosity measurements to ensure that all the pores are filled with the solution. After adding acids and bases to the solution and stirring the same ionic concentration is expected in the solution filled in the pores by diffusion of ions that is driven by concentration gradient. After being removed from the corrosion cells the samples were washed and dried at 115°C. The weight changes of the specimens after corrosion tests were measured using an electrobalance. The results are reported as weight loss/day to make the comparison between the results of test for different exposure times easier. The porosity of samples was measured by Archimedes' method using water immersion technique. Pore size distribution, porosity and surface area of membranes was measured by mercury porosimetry (Poresizer 9320, Micromeritics).

3. Results and discussion

3.1. Weight loss

Weight loss of the samples in acid solutions as a function of pH at room temperature and 80°C is shown in Fig. 1. Samples corroded at 80°C showed higher weight losses than those at RT. The higher weight losses of samples at 80°C can be attributed to the thermal activation of the reactions with 3Y–ZrO_2. Samples in HF solution showed low weight loss with no variation at all pHs both at RT and 80°C. The other samples except the one in HNO_3 solution, showed higher weight losses at pH 2. Low weight losses of samples in HF solutions can be attributed to the production of insoluble YF_3 on the surface that hinders further dissolution of yttrium. It must be noted that the lowest pH in solution of HF is around 3 since dissociation of hydrofluoric acid $HF \rightarrow H^+ + F^-$ takes place down to pH 3 and further addition of HF does not make any change in pH.

In basic solutions, the weight losses of samples increased when pH increased at RT and 80°C (Fig. 2). Weight losses of samples at 80°C were higher. The sample in water showed a weight loss in the same level as those in acid and basic solutions close to neutral pH, at pH 5 and 8.5 at 80°C. It indicated that the chemical reactions in highly acid and basic solutions caused the

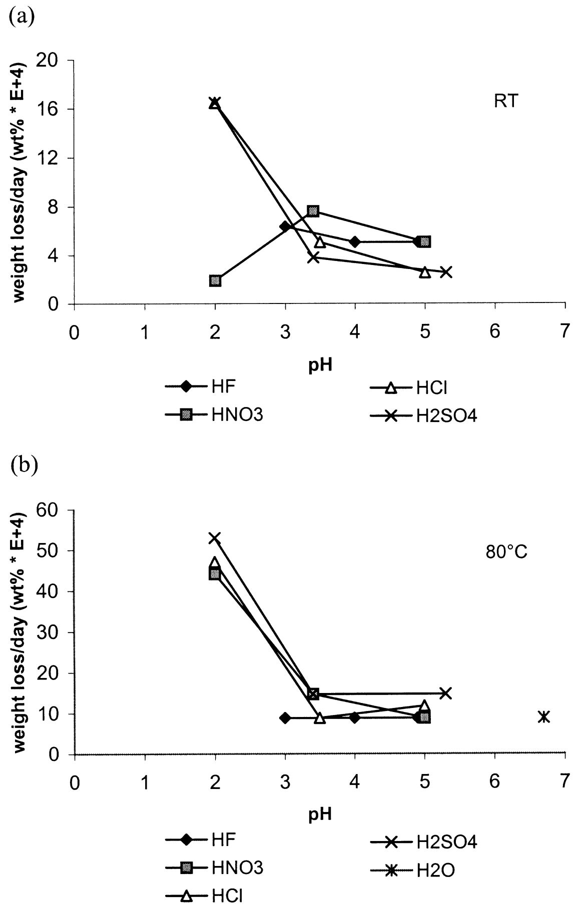

Fig. 1. Weight loss/day of HSY3 membranes in acid solutions at (a) room temperature, and (b) at 80°C.

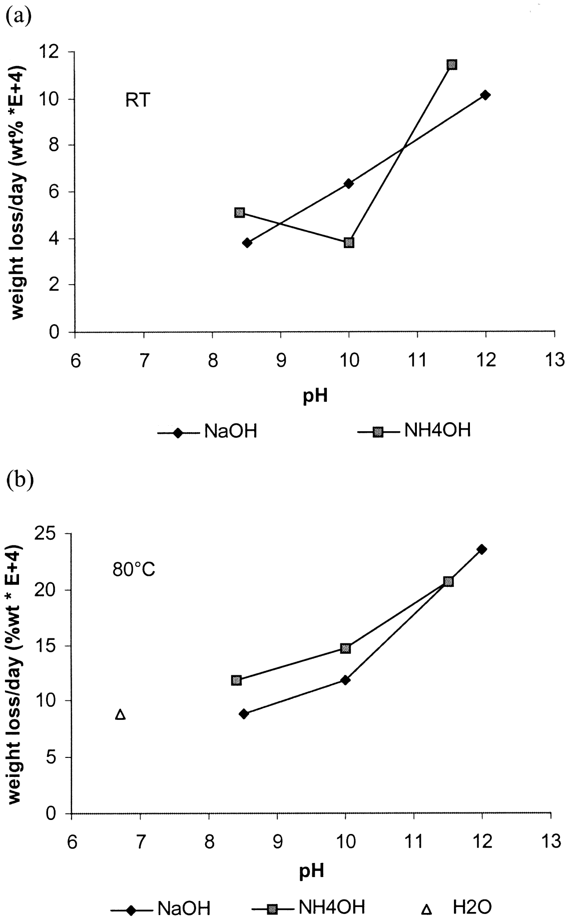

Fig. 2. Weight loss/day of HSY3 membranes in basic solutions at (a) room temperature, (b) at 80°C.

detected increase in weight loss. Samples in basic solutions showed lower weight losses than those in acid solutions.

It must be noted that although weight change is a widely used parameter to monitor the corrosion, it has some shortcomes in this case. It was measured after a certain period, assuming that weight change had a constant rate during corrosion, whereas this seldom happens; and it is common that the rates of attack diminish with time due to the formation of films of corrosion products. Dense and insoluble films inhibit weight loss, as in the case of sample in HF solutions, was found. It is also usually assumed that material is removed uniformly from the surface while a reagent often attacks selectively the grain boundaries which changes the properties dramatically without causing any remarkable weight change. Selective attack to silica in grain boundaries especially in basic solutions is an example for such case. Also, a small leaching of a minor constituent such as stabilizing agent, e.g. yttria in Y–TZP ceramics in acid solutions, may not be traceable in the weight change but introduces dramatic degradation. Lawson et al.[14] found no weight loss in acidic corrosion of dense samples of 3Y–TZP, while up to 80% m-phase was detected in those samples. It can be therefore misleading to use the weight change as a criterion of corrosion attack and it should be considered in a frame with the other results.

3.2. Phase composition

HSY3 membranes after sintering at 1200°C for 3 h had 100% tetragonal structure. The amount of monoclinic phase of membranes after corrosion in acid and basic solutions at RT and 80°C is shown in Figs. 3 and 4. A correlation between weight loss and phase transformation of samples after corrosion test was not found. Although the weight loss of samples in most cases was higher at pH 2, the phase transformation showed a peak at medium acidic pH of about 3.5 to 4 in acid solutions except the one in H_2SO_4.

Monoclinic content of samples in HF solutions increased at 80°C, compared to the values at RT and at both temperatures the highest amount of m-phase was found at the medium acidic pH around 4 while the weight loss showed no variation as a function of pH. Sample in water did not show any phase transformation. It indicates that chemical reactions destabilized the samples in other solutions.

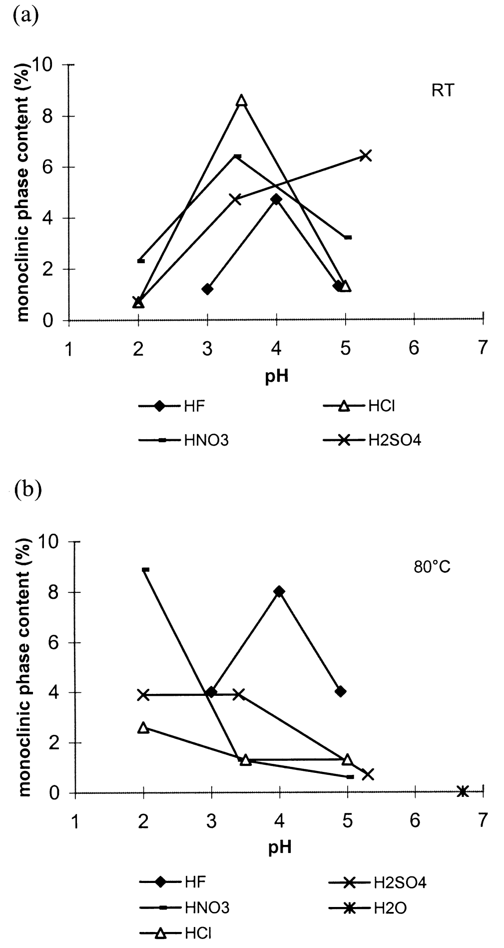

Fig. 3. The amount of monoclinic phase in HSY3 samples corroded in acid solutions at (a) RT for 79 days and (b) at 80°C for 34 days.

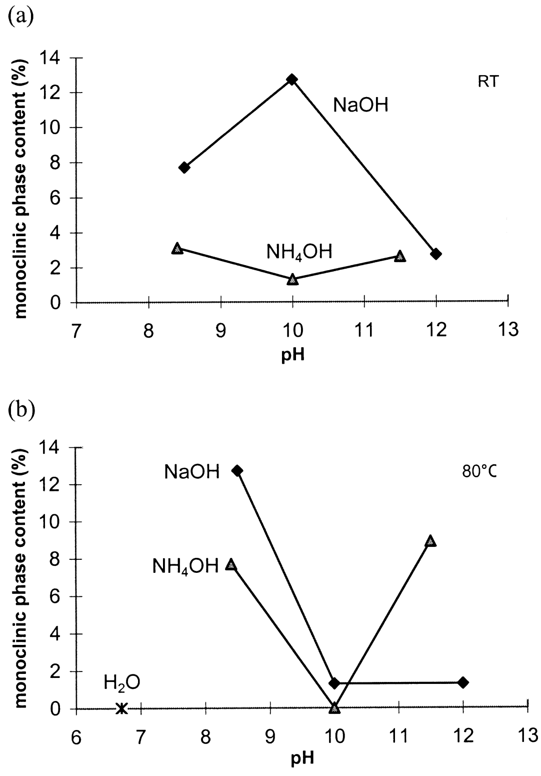

Fig. 4. The amount of monoclinic phase in HSY3 samples corroded in basic solutions at (a) RT for 79 days and (b) at 80°C for 34 days.

The highest phase transformation was found in the sample in NaOH solution at pH 8.5 that showed about 13% monoclinic phase at 80°C. Monoclinic content of samples in NaOH solutions was higher than those in NH_4OH at RT and 80°C except for the sample at pH 11.5 at 80°C. Phase composition showed the same trend in NH_4OH solution at RT and 80°C and m-phase was higher at 80°C. Small amount of m-phase was found at pH 10 in both samples at 80°C. Weight loss of the samples in these solutions did not correlate with the results of phase transformation.

The amount of m-phase of these samples in all cases was not more than 13% that is still relatively low value. It should be noted that in porous 3Y–TZP, phase transformation occurs also in the pore surfaces that are exposed to the corrosive solution.

3.3. Residual surface stress in corroded samples

Residual stress in the surfaces of samples was measured after corrosion test at 80°C. The change in lattice spacing measured by X-ray technique is associated to the state of stress in the samples. It is calculated as tensile stress when there is an increase in lattice spacing and as compressive stress, when the lattice spacing decreases. In most cases, increase of lattice spacing was detected in samples in acid and basic solutions that was detected as tensile stress in the samples after corrosion test at 80°C (Fig. 5). The level of stress was higher at pH 3–4, for samples in HF and HNO_3 solutions.

The unexposed sample had almost no stress (0.4±8.2 MPa). There are different sources of stress in the samples after corrosion test. Chemical stress caused by the chemical reactions in the aqueous system and mechanical stresses caused by t→m phase transformation due to the accompanied volume expansion or by the anisotropy of thermal expansion and thermal expansion mismatch of the phases.[16] Anisotropy in thermal expansion that is a source of shear stress is low in this case due to the low temperature of the test.

In aqueous media, water is adsorbed on the surface of the 3Y–ZrO_2 membrane and forms Y–OH and Zr–OH bonds. Migration of OH^- in the lattice results in the increase of lattice spacing and accumulates stress. The lattice expansion was detected as tensile stress, although the expansion of lattice was not caused by an external stress but it was due to the penetration of OH^- in the lattice. In contrast, penetration of OH^- ions in the lattice is believed to create compressive stress, due to the resistance of a rigid matrix.

Stressed zones provide nucleation points for phase transformation. When the monoclinic phase was produced, the compressive stress due to the volume expansion compensated the increase in lattice spacing, which was detected as tensile stress and resulted in low surface stress. As we can see in the samples with the highest amount of m-phase, the level of surface stress is low. To support this assumption, monoclinic phase was produced in the tetragonal structure of sintered sample by mechanical means (polishing the surface). The sample sintered at 1200°C had almost no surface stress. After polishing, about 18 MPa compressive stress was detected on the surface and a small peak of m-phase appeared in X-ray spectrum. It showed that the creation of small amount of m-phase introduced compressive stress to the surface. Micro-cracking also can release the accumulated stresses.

There is not a consensus on the mechanism of hydrothermal degradation, regarding the state of stress, before phase transformation and after the nucleation of m-phase. Based on the mechanism of hydrothermal attack suggested by Yoshimura et al.[17] diffusion of OH^- into the lattice creates a stressed zone and results in an increase in lattice spacing. Yashima et al.[18] also reported a reversible expansion and contraction of the zirconia lattice with ageing and subsequent annealing and they attributed it to the inclusion and exclusion of OH^- in the lattice. These findings support the interpretation of our results. Sato[19] on the other hand suggested that the formation of –OH bonds causes the release of strain which acts to stabilize tetragonal phase.

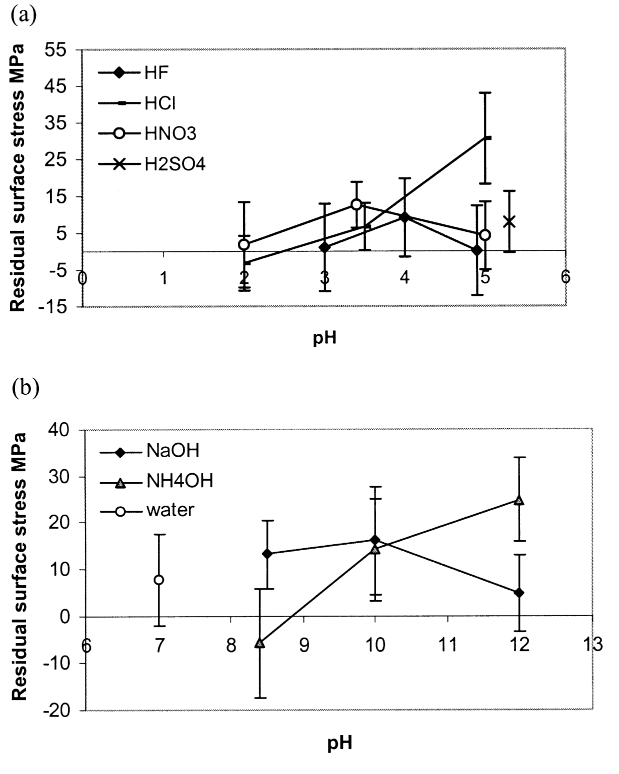

Fig. 5. Residual surface stress calculated from the changes in lattice spacing in samples after corrosion test at 80°C in (a) acidic and (b) water and basic solutions for 34 days.

Although this interpretation of the results of residual surface stress seems reasonable and explains some of the data, due to the complexity of the phenomena and other contributing parameters, it can not explain all the measured points. It must be noted that chemical corrosion stress that contributes to the measured surface stresses also varies in the samples exposed to different solutions at different pHs. Further investigation is needed to illuminate the contribution of different parameters in the resulting stress.

3.4. Porosity, pore size distributions and surface area

Porosity of the samples exposed to acid solutions at pH 2–3.4 and NH_4OH solution at pH 10, showed an increase to different extent from 1 to about 5% after the corrosion test at 80°C, except the one in HCl solution. Sample in HF/pH 3 showed about 1% increase in porosity. Samples in NH_4OH/pH 10 and in H_2SO_4/pH 2 showed higher increase in porosity after corrosion to about 5%. The median pore size values for these samples in acid solutions of pH 2–3.4 amounts approximately 130 nm except for H_2SO_4 at pH 2 and NH_4OH at pH 10 with values of about 160 and 155 nm, respectively. Higher increase in porosity and median pore size in the samples exposed to H_2SO_4/pH 2 and NH_4OH/pH 10 is in agreement with the results of weight loss in these samples.

Pore size distributions were narrow in samples corroded in different solutions (Fig. 6). The peak values of the distribution increased as compared to the distribution of the original membrane. Some of the pores in the lowest range of size 50–70 nm were not detected after the corrosion test. The removal of the finest pores from the pore size distribution curve was most likely due to the pore closure by corrosion products. Very fine pores are usually intra-agglomerate pores that may fill up readily during corrosion. In the upper range of pore sizes, there was no change.

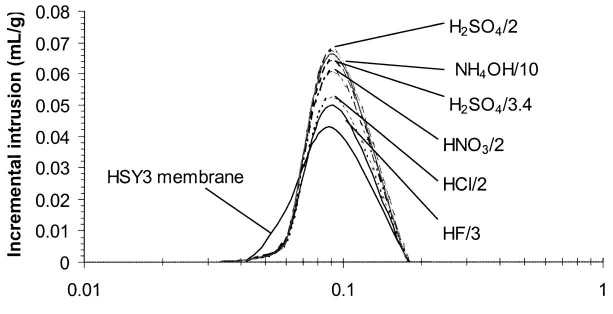

Fig. 6. Pore size distribution of membranes before and after the corrosion test in different solutions at 80°C.

Specific surface area of samples in HCl/pH 2 and HF/pH 3 after corrosion test at 80°C reduced from 2.4 (for unexposed sample) to 2 m^2/g. There was almost no change in surface area of sample in HNO_3 solution. Samples in H_2SO_4/pH 2 and 3.4 and the one in NH_4OH/pH 10 showed an increase in surface area to about 2.5 m^2/g. The increase in surface area arises mostly from the finer portion of pores that have a high ratio of area to volume. The filling of fine pores results in a decrease in surface area in samples exposed to HCl and HF solutions. On the other hand, surface area increases in samples after corrosion due to the increase in porosity and surface roughness. The resulting surface area reflects both of these counter-balancing effects.

3.5. Microstructure

Microstructural study of the samples with the highest monoclinic contents after corrosion test by SEM, showed no evidence of micro-cracks (Fig. 7). It indicates that the stresses introduced to the structure as a result of corrosion and volume change due to tetragonal to monoclinic phase transformation did not exceed the fracture strength. The lack of micro-cracks in these samples showed that the volume change associated with the phase transformation was absorbed in the porous structure. This fact also explains the low phase transformation in the samples corroded at 80°C. Although phase transformation initiated at room temperature but the lack of micro-cracks that opens new surfaces and assists the diffusion did not let the reaction front propagate from the surface to the interior.

3.6. Mechanism of degradation and the influencing factors

Different mechanisms have been proposed to explain the hydrothermal degradation of Y–TZP ceramics. Although so far no consensus has been reached, there is a good understanding of the parameters that influence the degradation. One of the proposed mechanisms of hydrohermal degradation is based on the chemical adsorption of OH^- ions at the surface that creates Zr–OH and Y–OH bonds. In the next step migration of OH^- in the lattice creates stressed zones that exceeds the energy barrier for tetragonal to monoclinic phase transformation.[11,19,20] Another mechanism of degradation is based on the depletion of stabilizing agent and nucleation of monoclinic phase from those sites. Shear strain and volume expansion associated with phase transformation produces cracks that provide new surfaces and further route for depletion of yttria. Microcracking therefore assists the diffusion of a slow ion like Y^{3+} as well as the faster ion OH^- in both of these mechanisms. When the phase transformation is low and does not cause cracking then the hydrothermal degradation is hindered due to kinetic factors.

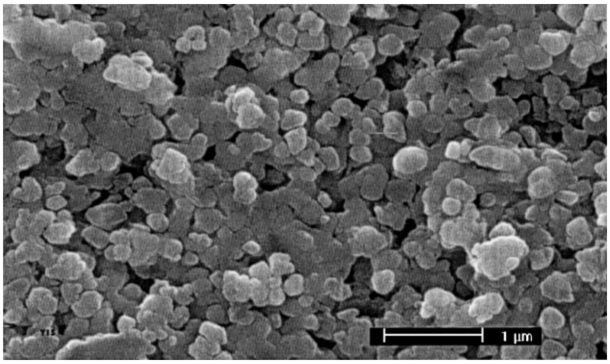

Fig. 7. SEM micrographs of sample in NaOH solution at pH 8.5, with the highest monocline content (13%) after corrosion at 80°C.

Material factors that influence the hydrothermal attack are grain size, yttria content, compositional factors (homogeneity and distribution of elements) and sintering temperature. There is a critical grain size for a given content of stabilizing agent (yttria) below which degradation does not occur. This critical grain size increases with the increase in yttria content and for 3 mol% Y–TZP it is about 0.3 μm for dense material.[21] The increase in yttria content in general, results in better stability of Y–TZP ceramics. There is also a range of temperature, in which phase transformation and degradation occurs and it depends on the yttria content and sintering temperature of Y–TZP. Ageing in water vapor and aqueous media accelerates the rate of reaction compared to ageing in air. Masaki[22] has reported that a density threshold exists (as a function of Y_2O_3 level and grain size), above which hydrothermal degradation will not occur. However this density for 3Y–TZP with a grain size of 0.2 μm aged in air at 200–250°C was about 5.8 g/cm^3 or 95% of the theoretical density which is well above the density of 3Y–TZP membranes.

The primary grain size of HSY3 powder was 0.1 μm, which is below the critical grain size reported for 3Y–TZP. Unlike in the dense parts, the lower sintering temperature applied for membrane implies less grain growth and lower compositional change in sintering process. In membrane, porosity that provides higher surface area in contrast with the dense parts enhances hydrothermal attack that initiates from the surface. Moreover, water solution containing corrosive ions enhanced the hydrothermal corrosion and dissolution of ions in the solution, resulted in an overall weight loss in the samples. On the other hand, low temperature, primary grain size smaller than the critical grain size and lack of micro-cracking in the samples were not in favour of severe hydrothermal attack and high amount of phase transformation. Good structural stability of HSY3 membrane in these solutions suggests the dominance of factors that hinder severe hydrothermal attack.

The difference between the results of phase transformation of sample in water from the other samples suggests the idea of competing corrosion mechanisms in corrosive solutions. Chemical reactions and ionic exchange in grain boundaries besides depletion of yttria play an important role. Chemical composition of the grain boundaries and distribution of impurities which depends on the powder processing route are far more important in corrosion of samples in aqueous solutions of acids and bases in contrast with the hydrothermal attack in water. It is assumed that high dissolution of a particular impurity in specific acid or basic solution may enhance phase transformation, whereas in another corrosive system remains intact. Detailed study of grain boundaries can illuminate the changes in grain boundaries as a result of corrosive attack.

4. Conclusions

Two mechanisms of hydrothermal attack were suggested in corrosion of 3Y–ZrO_2 membranes in aqueous solutions of acids and bases. Adsorption of OH^- on the surface and further penetration in the lattice, as well as depletion of yttria due to the dissolution were the dominant mechanisms. A weight loss was detected in corroded samples at room temperature and 80°C due to the dissolution of elements and other chemical reactions in aqueous solutions of acids and bases. The increase in temperature, almost in all cases resulted in higher weight loss due to the thermal activation of chemical reactions. Direct correlation was not found between weight loss and monoclinic phase content of samples after corrosion. The chemical resistance of 3Y–TZP microfiltration membranes was higher in highly basic aqueous media and the increase in temperature did not have a significant effect on the corrosion in basic solutions. Monoclinic to tetragonal phase transformation occurred at lower temperature (RT) in 3Y–TZP membranes compared to the dense counterpart. However, the monoclinic phase content of samples was not more than 13% in different solutions at RT and 80°C.

Residual surface stress in most cases was low. The increase in lattice spacing due to the penetration of OH ions in the lattice created stress zones for the nucleation of monoclinic phase. Following phase transformation compensated the increase in lattice spacing by the compressive stress resulting from the volume expansion due to tetragonal to monoclinic phase transformation. Porosity and median pore size of the samples increased after corrosion in acid and basic solutions to different extent. Pore size distribution of membranes after corrosion was narrow and showed the elimination of the finest pores. The surface area of the samples after corrosion test at 80°C increased except the samples in HF and HCl that showed a decrease in surface area. Micro-cracks were not found in the samples with the highest monoclinic content.

The results showed that unsupported microfiltration membrane produced from HSY3 powder exhibited a good structural stability and integrity in corrosive aqueous media at RT and 80°C, despite the porous structure and lower mechanical properties compared to the dense counterparts. It is attributed mostly to the primary grain size of powder lower than the critical grain size and lack of micro-cracking in the samples, due to phase transformation.

Acknowledgement

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