

# Corrosion of Zirconia Ceramics in Acidic Solutions at High Pressures and Temperatures

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## Abstract

Changes in microstructure and phase composition of ceria stabilized tetragonal zirconia polycrystals (Ce-TZP), magnesia and yttria partially stabilized zirconia [(Mg,Y)-PSZ] and magnesia partially stabilized zirconia (Mg-PSZ) were studied in diluted aqueous HCl, H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> solutions at a temperature of 390°C and a pressure of 27 MPa. Ce-TZP is corrosion resistant under these conditions in HCl, while Mg-PSZ is attacked severely and (Mg,Y)-PSZ undergoes a surface tetragonal to monoclinic phase transformation. All investigated zirconia ceramics suffer severe weight losses and transformation to the monoclinic phase on the surface in H<sub>2</sub>SO<sub>4</sub>. Only a small weight gain and a slight increase of m-phase on the surface of the ceramics is found in H<sub>3</sub>PO<sub>4</sub>. © 1999 Elsevier Science Limited. All rights reserved

## 1 Introduction

In the region of the critical point (22.1 MPa, 374°C), the physical properties of water change dramatically. At a pressure of 25 MPa and a temperature of 450°C the water density is 100 kg/m<sup>3</sup>, the values of the static dielectric constant and the ionic dissociation constant are 1.67 and 10<sup>-21.6</sup>, respectively. Values at ambient conditions are 1000 kg/m<sup>3</sup>, 80 and 10<sup>-14</sup>, respectively. As a result, nonpolar organic substances and oxygen are highly soluble in supercritical water, while inorganic salts precipitate. Thus, supercritical water is an ideal medium for the oxidation of organics, which are rapidly and quantitatively oxidized to CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O in the supercritical phase and inorganic salts can be separated simultaneously. Elements such as Cl, S or P are converted to the mineral acids HCl, H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>, respectively. This process is known as supercritical water oxidation (SCWO).<sup>1</sup>

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The major problem for the safe operation of SCWO is the corrosion of the reactor materials,<sup>2–4</sup> caused by the attack of the formed mineral acids. This problem can be minimized with improved reactor designs: reactors with a permeable liner<sup>5</sup> or transpiring walls<sup>6</sup> are developed. Zirconia based ceramics used as coating or liner is another possibility to protect the metallic reactor from corrosive solutions,<sup>7</sup> but only few experimental data are available on the corrosion of zirconia ceramics in SCWO environments. Hazlebeck et al reported<sup>8</sup> that a 9 mol% Y<sub>2</sub>O<sub>3</sub>-PSZ is rapidly corroded in mixtures of mineral acids without giving any numerical data. Morin<sup>9</sup> found that Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub> experienced cracking in acidic, neutral and caustic aqueous systems at 28.2 MPa and 450°C. This behaviour is caused by the transformation from metastable tetragonal (t) to monoclinic (m) phase. Boukis et al.<sup>10</sup> found that Mg-PSZ and (Mg,Y)-PSZ are corrosion resistant in water containing HCl and O<sub>2</sub> at 25 MPa and 465°C. Y-TZP and Y-PSZ cracked and disintegrated due to t→m phase transformation. This is in accordance with the experimental data reported at lower temperatures and pressures.<sup>11–14</sup>

## 2 Experimental Procedures

### 2.1 Preparation of the ceramic test

Samples of Ce-TZP were prepared by uniaxial and cold isostatic pressing of 12Ce-TZP powder (Tosoh Inc., Japan) at 32 and 800 MPa, respectively, followed by sintering at 1600°C for 2 h. The material consisted of 100% t-phase after sintering.

(Mg,Y)-PSZ was prepared from commercially available powders of 3Y-TZP (Tosoh Inc., Japan), 10.2 mol% MgO-ZrO<sub>2</sub> (MEL Chemicals, UK) and MgAl<sub>2</sub>O<sub>4</sub> (Condea Ceralox).<sup>15</sup> The mixture was attrition milled in ethanol for 4 h, wet sieved and dried. The powder was compacted by uniaxial pressing (50 MPa) and cold isostatic pressing (500 MPa). The green bodies were sintered in air at

1720°C for 20 min, cooled at 6°C/min to 1400°C, annealed for 1.5 h and cooled then at 15°C/min to room temperature. The m-phase content of polished specimens was 15 vol%.

Commercially available Mg-PSZ (FZM, Friatec AG, Germany) was used as third material. The amount of m-phase on the polished surface was 8–9 vol%.

The ceramic discs were cut into bars (25×9×4 mm) and polished to a mirror-like surface using 1 µm diamond paste.

## 2.2 Corrosion experiments

For corrosion tests a recently patented tube reactor<sup>16</sup> was scaled up to an inner diameter of 12 mm. Supercritical water containing 0.1 mol/kg<sup>1</sup> HCl, H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub> was used as corrosive agent. The test specimens were maintained in the reactor at 27 MPa and 390°C for 50 h. The interest was focused on this temperature, because the corrosion of metallic alloys proceeds fast near temperatures below the density drop and leads to failure of the reactor after few hours.<sup>2–4</sup> At 27 MPa, the density drop is below 400°C.

## 2.3 Analytical methods

The phases were identified by X-ray diffraction analysis (XRD, Philips PW 1729) on the polished surfaces before and after the corrosion experiments. The content of m-phase was determined by

the method of Garvie and Nicholson.<sup>17</sup> Surface analysis of the corroded specimens was performed with scanning electron microscopy (SEM, LEO Gemini 982) and energy-dispersive X-ray analysis (EDX, Oxford).

## 3 Results and discussion

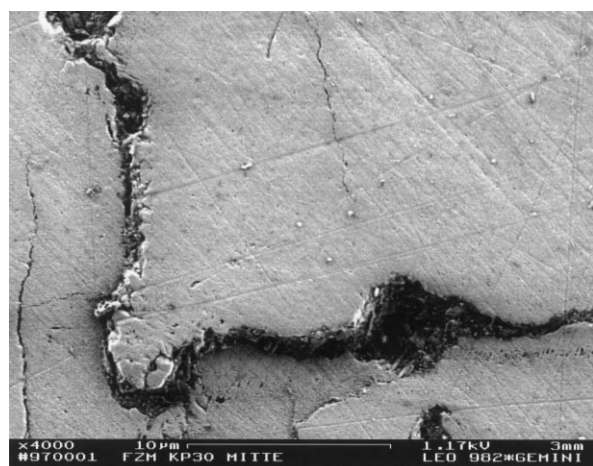
A compilation of the results of weight change and XRD measurements is given in Table 1. In Mg-PSZ, (Mg,Y)-PSZ and Ce-TZP XRD-analysis (90%, Cu-K<sub>α</sub>-radiation at 2θ = 28°) gives structural information about the first 9.6, 9.75 and 6.5 µm of the samples, respectively.

### 3.1 Hydrochloric acid

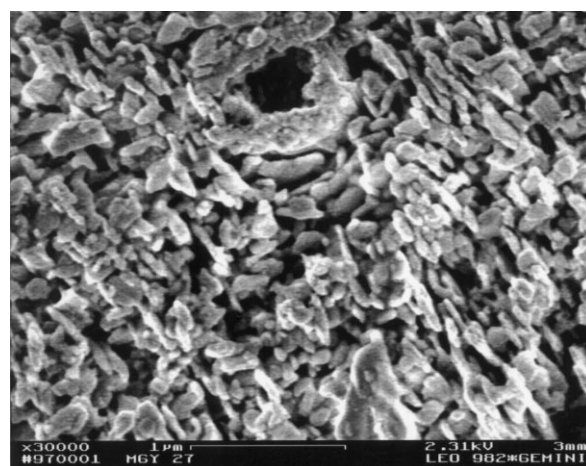
Mg-PSZ is susceptible to corrosive attack in supercritical water containing HCl. Corrosion starts at the partially glassy grain boundaries (Fig. 1) and is supported by the presence of a forsterite (Mg<sub>2</sub>SiO<sub>4</sub>)-rich grain boundary phase. Almost complete transformation to the monoclinic phase at the surface was determined after only 50 h of exposure. The accompanying, mostly inter-crystalline microcracking let the corrosive solution penetrate into the bulk of the specimen leading to dissolution of magnesium there. This caused t→m transformation in the bulk of the ceramic and disintegration of the ceramic specimen. (Mg,Y)-PSZ is,

**Table 1.** Weight change and m-phase content on the surface of zirconia ceramics exposed to the acidic solutions for 50 h at 390°C and 27 MPa

Material	HCl			H <sub>2</sub> SO <sub>4</sub>			H <sub>3</sub> PO <sub>4</sub>		
	Ce-TZP	Mg,Y-PSZ	Mg-PSZ	Ce-TZP	Mg,Y-PSZ	Mg-PSZ	Ce-TZP	Mg,Y-PSZ	Mg-PSZ
Weight change (mg/cm <sup>-2</sup> )	< -0.1	+0.3	-1.0	-52.3	-4.5	-6.6	+0.1	+0.1	+0.2
m-phase (vol%)	< 2	31	93	33	92	98	< 2	18	11



**Fig. 1.** Grain boundary attack on the surface of Mg-PSZ (HCl, 50 h, 390°C/27 MPa).



**Fig. 2.** Corroded surface of (Mg,Y)-PSZ (HCl, 50 h, 390°C/27 MPa).

presumably due to the lower silicate content of the grain boundary phase, more resistant to hydrochloric acid than Mg-PSZ. Spinel particles at the surface of the tested specimens are dissolved (Fig. 2). Since the powder used for the fabrication of the Ce-TZP ceramic was silicate-poor (70 ppm SiO<sub>2</sub>), no silicate-rich grain boundary phase can be formed. The tested specimens retained tetragonal phase completely and no change in microstructure could be detected.

### 3.2 Sulfuric acid

Sulfuric acid is the most aggressive of the investigated corrosive agents. Mg-PSZ and (Mg,Y)-PSZ suffer severe weight losses and total transformation to the monoclinic phase on the surface. Corrosion starts at the grain boundaries, spreading out fastly to the neighbouring grains. Magnesium is selectively dissolved due to its higher alkaline character and leaves a polycrystalline layer of m-ZrO<sub>2</sub> on the surface. However, the penetration depth of sulfuric acid into the bulk of these ceramics is low. Also Ce-TZP suffers severe degradation when subjected to the H<sub>2</sub>SO<sub>4</sub> (Fig. 3). The degradation of Ce-TZP in sulfuric acid could be referred to the dissolution of a ceria surface layer on the TZP grains combined with a t→m phase transformation on the surface. This leads to fast penetration of the ceramic bulk (500 μm in 50 h), washing out of grains and degradation. Cerium is not dissolved from the grains presumably due to its low mobility in the zirconia lattice at this temperature.

### 3.3 Phosphoric acid

H<sub>3</sub>PO<sub>4</sub> is less corrosive than HCl and H<sub>2</sub>SO<sub>4</sub> for all three zirconia ceramics. A small weight gain due to the formation of zirconium phosphates could be measured. These corrosion products inhibit further surface attack, so only a slight increase of m-phase on the surface is measured.

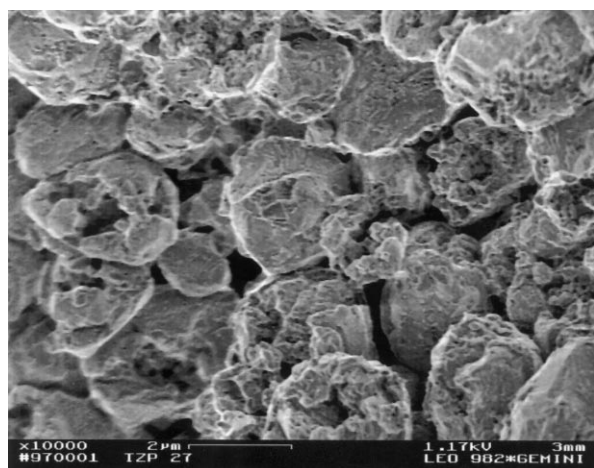


Fig. 3. Grains on the surface of Ce-TZP (H<sub>2</sub>SO<sub>4</sub>, 50 h, 390°C/27 MPa).

## 4 Conclusions

At a pressure of 27 MPa and a temperature of 390°C, aqueous sulfuric acid is the most aggressive environment for the tested zirconia ceramics. Severe weight losses and decomposition into m-ZrO<sub>2</sub> on the surface are found. Corrosion in hydrochloric acid is strongly dependent on the composition of the grain boundary phase. Extremely negative for the corrosion resistance is the presence of a silicate-containing glassy phase on the grain boundaries. H<sub>3</sub>PO<sub>4</sub> is less corrosive than HCl or H<sub>2</sub>SO<sub>4</sub> due to the formation of zirconium phosphates on the surface of the zirconia ceramics which inhibits further corrosion.

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