



Letter to the Editors

Phase transformation of stabilised zirconia in water and 1.0 M LiOH

M. Oskarsson^a, E. Ahlberg^{b,*}, K. Pettersson^a^a *Department of Materials Science and Engineering, Royal Institute of Technology, SE-10044 Stockholm, Sweden*^b *Department of Chemistry, Göteborg University, SE-41296 Göteborg, Sweden*

Received 5 October 2000; accepted 10 January 2001

Abstract

The phase transformation of stabilised zirconia was studied after exposure to water and lithiated (1 M LiOH) water for 3 days at 400°C, with the aim to evaluate a proposed reason for the enhanced Zircaloy corrosion observed in the presence of lithium hydroxide. Three different tetragonal zirconia samples were investigated, stabilised by addition of yttrium, cerium and by small crystallite size, respectively. One stabilised cubic zirconia sample, with addition of calcium, was also included in the investigation. The corrosion test was performed in mini autoclaves and the crystal structure of the material, before and after the autoclave test, was characterised with X-ray diffraction. For the three zirconia versions with tetragonal phase, a majority of the material transformed to monoclinic phase in both environments, i.e., the transformation rate was found to be independent of the presence of lithium hydroxide. The fraction transformed to monoclinic zirconia was about 63% for size-stabilised sample and 84–94% for the yttria- and cerium-stabilised zirconia, while the cubic zirconia was unaffected by the corrosion test. Based on our result no evidence of preferential dissolution of stabilised zirconia is found in LiOH solution, compared to test in pure water. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Lithium hydroxide is added to control the pH-value in pressurised water reactors (PWR). However, localised boiling may increase the concentration of LiOH to detrimental levels, resulting in an enhanced corrosion rate for the fuel cladding [1]. Different theories have been proposed to explain the harmful effect of lithium hydroxide such as: enhanced oxygen diffusion either by incorporation of lithium ions in the oxide phase [2] or by formation of Zr–OLi surface groups [3], and generation of porosity by formation of Li₂O from the Zr–OLi surface groups [3] or by preferential dissolution of cubic or tetragonal crystallites in the oxide [4–6].

The purpose of the present work was to investigate the phase transformation of different stabilised zirconia

under conditions that are similar to corrosion tests of zirconium-based alloys. A comparison between the behaviour in pure and lithiated water will reveal if preferential dissolution of tetragonal/cubic phase in LiOH solutions can be a reasonable explanation to the enhanced corrosion kinetics.

Preferential dissolution of yttria-stabilised zirconia (YSZ) single crystals at 600°C to 780°C under 100 MPa has been reported [7]. The YSZ were reported to be partly dissolved and reprecipitated as the monoclinic phase in LiOH solutions (15% and 30%), while for neutral water the sample remained unchanged. These findings were used by Cox et al. to explain experimental results on pre-oxidised Zircaloy-2 samples, which were tested in 300°C water for 3 days and then transferred to 0.1 M LiOH solution at the same temperature [5]. The oxide surface was investigated before and after oxidation in LiOH solution, and pores are reported to develop after exposure in 0.1 M LiOH. Also test in 1.0 M LiOH was performed and a development of deep porosity was found [5].

* Corresponding author. Tel.: +46-31 772 2879; fax: +46-31 772 2853.

E-mail address: ela@inoc.chalmers.se (E. Ahlberg).

YSZ is, however, sensitive to water and water-solutions and an uncontrolled phase transformation from cubic/tetragonal to monoclinic may occur at some conditions. For example, such a phase transformation occurs at low temperature ($\leq 200^\circ\text{C}$) and normal pressure water [8]. Also on partially YSZ the tetragonal phase on the surface is transformed to monoclinic phase by annealing in water at $65\text{--}120^\circ\text{C}$ [9]. It is suggested that the chemical reaction between water and Zr–O–Zr bonds on the surface gives rise to OH-groups, which enhances the crack growth in zirconia and controls the transformation rate. For size-stabilised tetragonal zirconia a phase transformation occurs even at room temperature and is explained by changes in the surface energy upon adsorption of water [10].

2. Experimental

Mini autoclave tests were performed in water and in 1.0 M LiOH at 400°C and 10 MPa for 3 days. Four different versions of stabilised zirconia were tested:

1. YSZ, which is a commercial specimen, delivered as small plates.
2. Calcium-stabilised ZrO_2 with a chemical composition of 95% ZrO_2 and 5% CaO is a commercial product and was delivered as a tube.
3. Cerium-stabilised ZrO_2 was prepared from $\text{Zr}(\text{NO}_3)_4$ -solution. When the solution is heated to 700°C , the water is first evaporated and then the $\text{Zr}(\text{NO}_3)_4$ decomposes to ZrO_2 . The produced material appears as a coarse-grained powder.
4. Crystallite size-stabilised ZrO_2 was produced by reacting zirconium tetrachloride (ZrCl_4) with steam, and contains some residual chloride.

The crystal structure was characterised with a Philips X-ray diffractometer, using $\text{CuK}\alpha$ radiation. To calculate the fraction between the tetragonal (1 1 1) and monoclinic (1 1 1) and (1 1 $\bar{1}$) were compared according to [11,12]

$$V_m = \frac{1.311X_m}{(1 + 0.311X_m)}, \quad (1)$$

where

$$X_m = \frac{\{I_m(1\ 1\ 1) + I_m(1\ 1\ \bar{1})\}}{\{I_t(1\ 1\ 1) + I_m(1\ 1\ 1) + I_m(1\ 1\ \bar{1})\}}, \quad (2)$$

V_m is the monoclinic volume fraction, I_m the peak integral intensity of monoclinic phase and I_t the peak integral intensity of tetragonal phase.

3. Results and discussion

The YSZ (I) has mainly a tetragonal structure but with a detectable amount of the monoclinic phase, Fig. 1(a). It is readily transformed to the monoclinic phase in both water and lithiated water, Figs. 1(b) and (c), and the fraction of monoclinic phase after test was similar for the two environments, Table 1. The corrosion

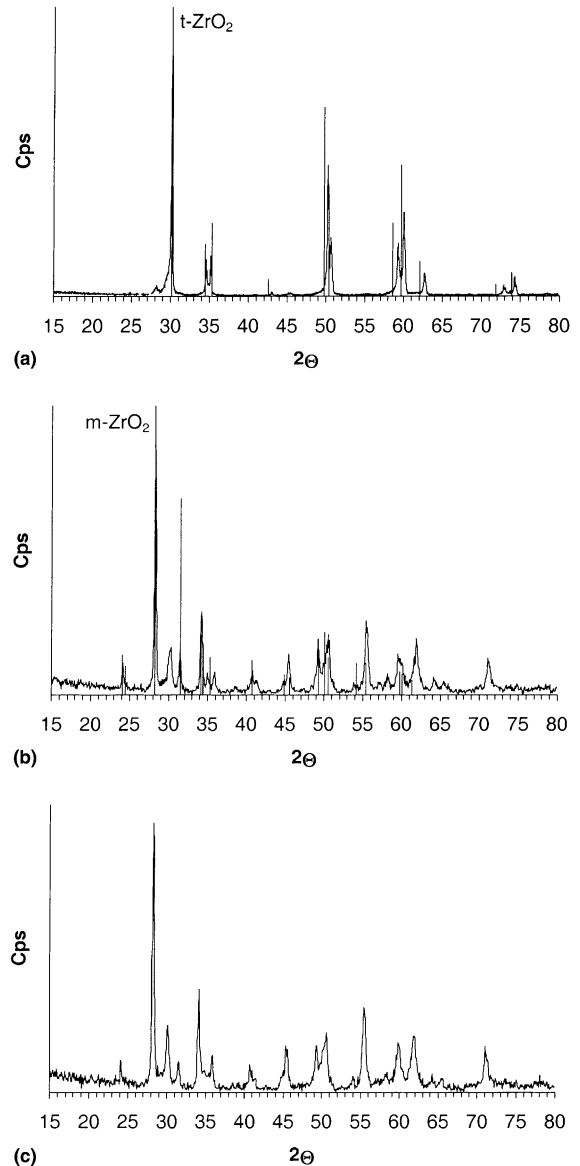


Fig. 1. X-ray diffraction of YSZ (I): (a) reference sample with the standard reflections for tetragonal ZrO_2 ; (b) sample tested in H_2O at 400°C , 10 MPa for 3 days with the standard reflections for monoclinic ZrO_2 ; (c) sample tested in 1.0 M LiOH at 400°C , 10 MPa for 3 days.

Table 1
Fraction of monoclinic zirconia phase, after autoclave test

| Material | Environment | Monoclinic (%) |
|---------------------------------------|------------------|----------------|
| Y-ZrO ₂ (I) | H ₂ O | 90 |
| Y-ZrO ₂ (I) | Li | 87 |
| Ce-ZrO ₂ (III) | H ₂ O | 94 |
| Ce-ZrO ₂ (III) | Li | 84 |
| Size-stabilised ZrO ₂ (IV) | H ₂ O | 64 |
| Size-stabilised ZrO ₂ (IV) | Li | 62 |

test resulted also in a visible transformation of the sample from plate to powder, but the former sides of the plate were relatively intact. These results are in accordance with the sensitivity of YSZ for water at relatively low temperatures [8,9,13]. Under the test conditions used in the present investigation the transformation rate is independent of the presence of lithium hydroxide. Hence, the large difference observed at high temperatures [7] is difficult to explain.

The ZrO₂ with calcium (II) is fully stabilised to the cubic phase, see Fig. 2(a). The material was shown to be inert to exposure to water and lithiated water, since no phase transformation was observed, Figs. 2(b) and (c).

Quantitative chemical analysis of the cerium-stabilised ZrO₂ (III) material in a JEOL 840 SEM, equipped with a Oxford Isis EDS-system, showed the presence of 2.15% cerium and 0.85% hafnium in the zirconia matrix. The material has a tetragonal phase structure as determined by X-ray diffraction, Fig. 3(a). Surprisingly, for this material a larger fraction was transformed to the monoclinic phase in water than in lithiated water, see Figs. 3(b), (c) and Table 1. In both environments the material undergoes a visible change from coarse- to fine-grained powder.

The crystallite size-stabilised ZrO₂ (IV) powder was investigated with transmission electron microscopy (JEOL 2000EX). The crystallite size was shown to be 10–20 nm and selected area diffraction indicates mainly tetragonal crystal structure. It is well-known that a small crystallite size of the oxide grains stabilises the tetragonal phase (<30 nm) [14,15]. X-ray diffraction analysis of the powder also shows a tetragonal phase structure with a small amount of the monoclinic phase, see Fig. 4(a). Also for this material the fraction transformed to the monoclinic phase is similar for the two environments, see Figs. 4(b), (c) and Table 1. Furthermore, this material has the lowest transformation rate of the materials tested. Both autoclave tests resulted in an agglomeration for a fraction of the powder. This is in accordance with the significant decrease in surface area observed after exposure to water vapour at 350°C [10].

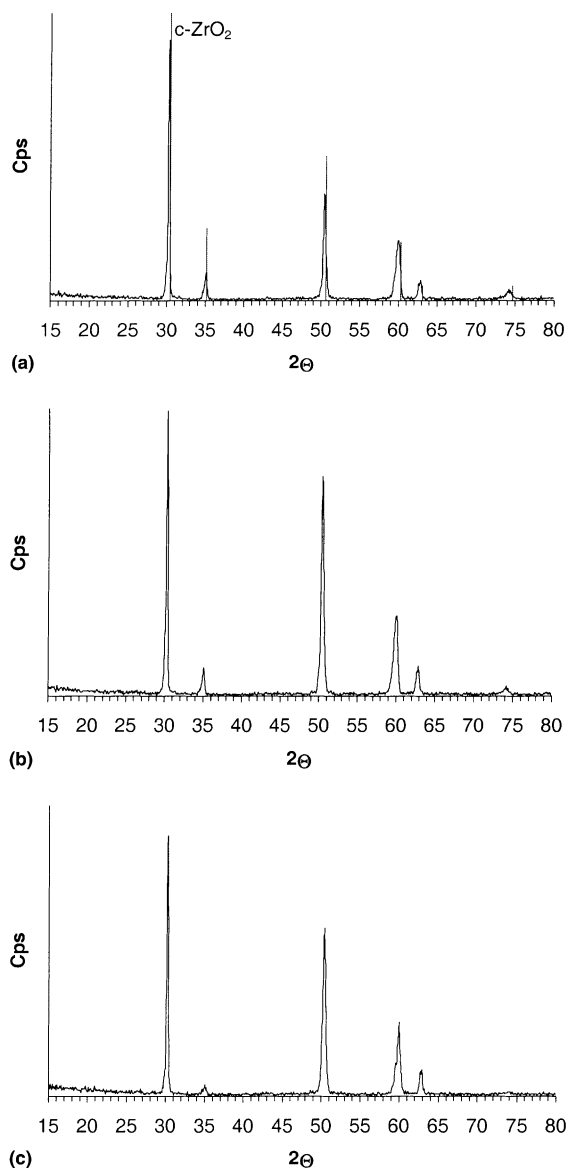


Fig. 2. X-ray diffraction of calcium-stabilised zirconia (II): (a) reference sample with the standard reflections for cubic ZrO₂; (b) sample tested in H₂O at 400°C, 10 MPa for 3 days; (c) sample tested in 1.0 M LiOH at 400°C, 10 MPa for 3 days.

The presence of a second element as a stabiliser of the high temperature phase seems to have a pronounced effect on the phase transformation and it is therefore doubtful to base theories regarding Zircaloy corrosion on the performance of these materials. However, the size-stabilised sample resembles more the tetragonal fraction of the oxide formed on Zircaloy in autoclave tests and therefore the results obtained for this material can be used for discussion of Zircaloy corrosion. The

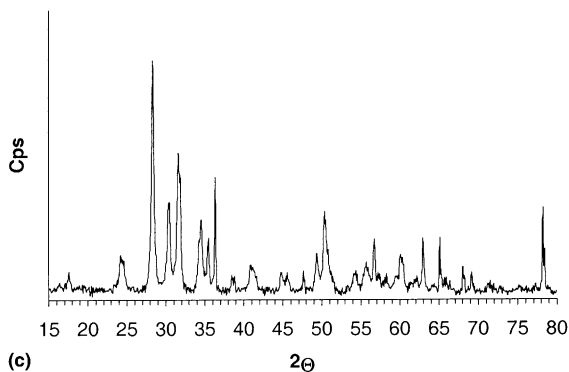
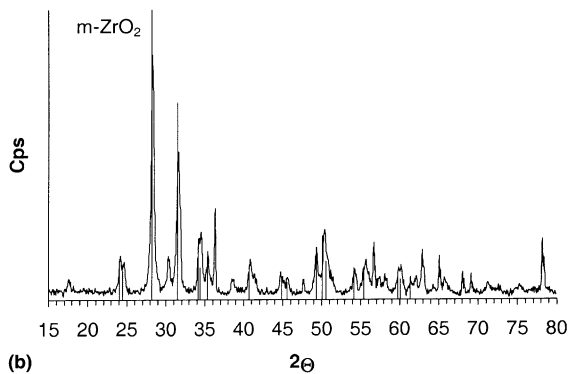
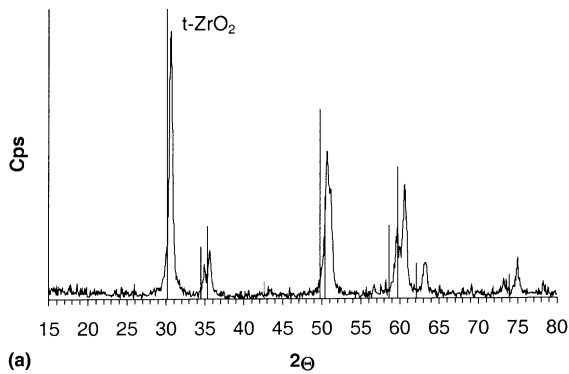


Fig. 3. X-ray diffraction of cerium-stabilised zirconia (III): (a) reference sample with the standard reflections for tetragonal ZrO_2 ; (b) sample tested in H_2O at $400^\circ C$, 10 MPa for 3 days with the standard reflections for monoclinic ZrO_2 ; (c) sample tested in 1.0 M LiOH at $400^\circ C$, 10 MPa for 3 days.

fact that the phase transformation rate is similar in water and lithiated water rules out the possibility of preferential dissolution as a cause for the increased porosity obtained in lithium hydroxide solutions [5]. On the basis of the present results it seems reasonable to look for other causes of the LiOH-effect than preferential dissolution of tetragonal or cubic oxide phase [16,17].

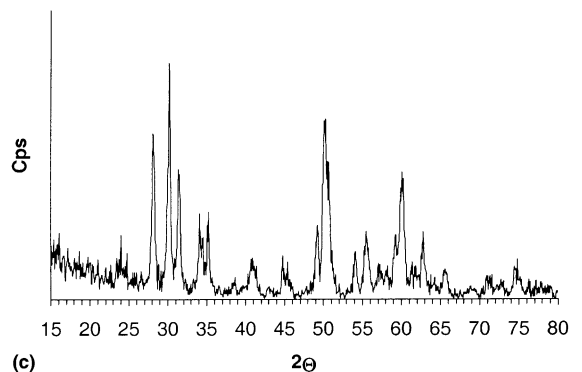
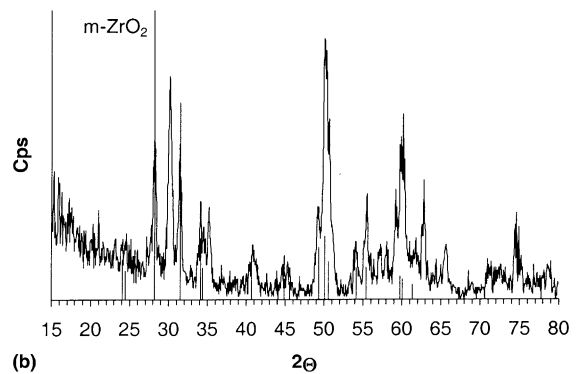
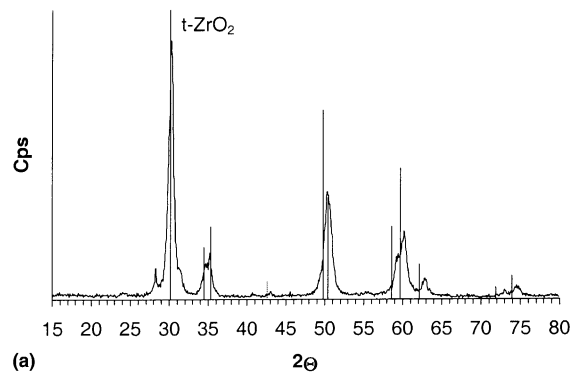


Fig. 4. X-ray diffraction of crystallite size stabilisation of zirconia (IV): (a) reference sample with the standard reflections for tetragonal ZrO_2 ; (b) sample tested in H_2O at $400^\circ C$, 10 MPa for 3 days with the standard reflections for monoclinic ZrO_2 ; (c) sample tested in 1.0 M LiOH at $400^\circ C$, 10 MPa for 3 days.

4. Conclusions

Based on our result no evidence for preferential dissolution of stabilised zirconia is found in LiOH solution, since the behaviour of the different oxides was the same in both environments.

The phase transformation from tetragonal/cubic to monoclinic zirconia depends strongly on the nature of

the stabilising element. Thus, such compounds are not proper reference materials for evaluation of the mechanism of Zircaloy corrosion.

Acknowledgements

Financial support from the Swedish Nuclear Power Inspectorate (SKI) is gratefully acknowledged. This work was carried out as a part of the Swedish research programme for the understanding of Zircaloy corrosion and hydriding mechanisms, funded by ABB Atom AB, Barsebäck Kraft AB, OKG AB, and Vattenfall.

References

- [1] H. Coriou, L. Grall, J. Meunier, M. Pelras, H. Willermoz, *J. Nucl. Mater.* 7 (1962) 320.
- [2] E. Hillner, J.N. Chirigos, The Effect of Lithium Hydroxide and Related Solutions on the Corrosion Rate of Zircaloy in 680 F Water, Bettis Atomic Power Lab., Pittsburgh, PA, Contract AT-11-1-GEN-14, 1962.
- [3] N. Ramasubramanian, N. Precoanin, V.C. Ling, in: L.F.P.V. Swam, C.M. Eucken, (Eds.), *Zirconium in the Nuclear Industry: Eighth International Symposium*, vol. ASTM STP 1023, Philadelphia, PA, 1989, p. 187.
- [4] B. Cox, Y.-M. Wong, in: C.M. Eucken, A.M. Garde, (Eds.), *Zirconium in the Nuclear Industry: Ninth International Symposium*, vol. ASTM STP 1132, Kobe, Japan, 1991, p. 643.
- [5] B. Cox, C. Wu, *J. Nucl. Mater.* 199 (1993) 272.
- [6] B. Cox, M. Ungurela, Y.-M. Wong, C. Wu, in: E.R. Bradley, G.P. Sabol, (Eds.), *Zirconium in the Nuclear Industry: 11th International Symposium*, vol. ASTM STP 1295, Garmisch-Partenkirchen, Germany, 1996, p. 114.
- [7] M. Yoshimura, T. Hiuga, M. Shimada, *J. Am. Ceram. Soc.* 69 (1986) 583.
- [8] F. Meschke, G.D. Portu, *J. Europ. Ceram. Soc.* 11 (1993) 481.
- [9] T. Sato, M. Shimada, *J. Am. Ceram. Soc.* 68 (1985) 356.
- [10] S.B. Xie, E. Iglesia, A.T. Bell, *Chem. Mater.* 12 (2000) 2442.
- [11] C. Garvie, P.S. Nicholson, *J. Am. Ceram. Soc.* 56 (1972) 303.
- [12] H. Toroya, M. Yoshimura, S. Somiya, *J. Am. Ceram. Soc.* 67 (1984) 119.
- [13] Y.S. Kim, S.C. Kwon, *J. Nucl. Mater.* 270 (1999) 165.
- [14] C. Garvie, *J. Phys. Chem.* 69 (1965) 1238.
- [15] P. Barberis, *J. Nucl. Mater.* 226 (1995) 34.
- [16] Y.H. Jeong, J.H. Baek, S.J. Kim, H.G. Kim, H. Ruhmann, *J. Nucl. Mater.* 270 (1999) 322.
- [17] M. Oskarsson, E. Ahlberg, K. Pettersson, this issue, p. 97.