Available online at www.sciencedirect.com

ScienceDirect

Journal of Nuclear Materials 360 (2007) 92–98

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Kinetics of hydrothermally induced transformation of yttria partially stabilized zirconia

J.J. Payyapilly, D.P. Butt *

Materials Science and Engineering Department, University of Florida, Gainesville, FL 32611, USA

Received 19 August 2004; accepted 25 August 2006

Abstract

Yttria-stabilized zirconia undergoes tetragonal to monoclinic phase transformation under hydrothermal conditions in the temperature range of 150–350 °C. Phase transformation accompanied by volume change in bulk yttria partially stabilized zirconia (YPSZ) leads to micro-cracking, loss of mechanical integrity and ultimately disintegration. The mechanical properties of the bulk YPSZ material deteriorate with the amount of the phase transformation and in some cases catastrophic failure are observed. The phase transformation is analyzed using macroscopic and microscopic techniques. X-ray diffraction data is used to quantify the phase transformation in bulk material. Kinetics of the phase transformation is studied at various temperatures.

1. Introduction

Zirconia has a wide range of useful attributes and potential applications based on the excellent mechanical properties such as high toughness and good strength [1]. Zirconia exhibits good thermal stability within a wide range of temperatures making it a suitable candidate for structural and thermal applications in the nuclear industry. Zirconia is used as electrodes and fuel cells based on the electronic and ionic conducting properties of the material.

Zirconia exists in three well-defined polymorphic forms: monoclinic, tetragonal and cubic phases. The monoclinic phase is thermodynamically stable till temperatures ~1240 °C, the tetragonal phase is stable between ~1440 °C and ~2340 °C and the cubic phase is stable up to the melting point at ~2340 °C [2]. Pure zirconia has been of limited use as a high temperature structural ceramic because of the relative ease with which it transforms from tetragonal to monoclinic phase at ~1240 °C. The transformation from tetragonal to monoclinic phase is a diffusionless process with an associated volume expansion of ~4% [3]. The significant volume change during the transformation process causes the bulk zirconia material to fail catastrophically. Small amounts of yttria, calcia and other additives are added to zirconia to stabilize the tetragonal phase at temperatures lower than 1240 °C and

---

* Corresponding author. Present address: Materials Science and Engineering, 302 K, Micron Engineering Center (MEC), Boise State University, 1910 University Dr., Boise, IS 83725-2075, USA. Tel.: +1 208 426 1054; fax: +1 208 426 2470.

E-mail address: darrylbutt@boisestate.edu (D.P. Butt).

0022-3115/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2006.08.027

prevent the transformation of tetragonal to monoclinic phase. Partially stabilized zirconia has improved shock resistance and toughness compared to unstabilized zirconia [4]. Zirconia is stable until 950 °C at ambient conditions [5]. However, in the presence of water or water vapor, partially stabilized zirconia can transform from the tetragonal to the monoclinic phase at elevated temperature of 120–150 °C [5]. During the transformation of the tetragonal to monoclinic phases, cracks form on the surface of the YPSZ samples due to the volume change accompanied by the phase transformation. Cracks further propagate towards the interior of the sample causing the sample to fail catastrophically. The kinetics of transformation and the failure mechanism is not well understood and is not reported in literature.

2. Experimental procedure

YZ-110 HS YPSZ samples, which are the high strength version of standard NORZIDE™ YZ-110 HS YPSZ provided by Saint Gobain Inc., were used for the current study. YPSZ samples were exposed to various hydrothermal conditions in an autoclave as shown in Table 1. The exposed cylindrical samples were 1 cm long and had a diameter of 1 cm. The density of the samples was 6.07 g/cc and the Youngs modulus was 207 GPa. The samples contained 4.7 mol% of yttria and measured a hardness of 12.2 GPa before the samples were exposed to hydrothermal conditions. The grain size of the samples was approximately 1 μm. Porosity was negligible in the samples.

Two identical samples were treated in the autoclave during each hydrothermal exposure. One of the samples was used for the X-ray measurements and the other was used for microscopy and hardness measurement. The thickness of the transformed layer in the treated samples was measured using optical microscopy.

The autoclave (Autoclave Engineers model number 401 A-9444 and the serial number of the vessel is 01150761-1) used for the hydrothermal treatment of the samples consisted of a high pressure vessel made of 316 SS (stainless steel) and fittings to pressurize water at high temperature and pressure. The vessel was designed to hold gases at 350 °C and 20.68 MPa pressure. The inner and outer surface temperatures of the vessel were monitored using K type thermocouples. The thermocouple that measured the sample temperature was fitted into the vessel such that the lower tip of the thermocouple was placed near the top surface of the sample in the sample holder. The vessel was heated at 3 °C/min for each hydrothermal treatment.

Table 1
Hardness measurements on untreated and hydrothermally treated YPSZ

Sample exposure			Average hardness H_V (GPa)
As received			12.2
Temperature (°C)	Pressure (MPa)	Time (h)	
300	13.79	24	7.6
250	8.27	12	6.5
200	2.07	12	7.7
300	2.07	12	7.5
250	2.07	12	8.3
200	2.07	12	9.2
180	2.07	12	9.8
150	–	12	11.3
120	–	12	13
100	–	12	12.6
180	2.07	24	8.6
180	2.07	48	8.5
180	2.07	72	8.4
180	2.07	96	7.7
150	–	72	12

Deionized water (pH ≈ 6) was used to pressurize the autoclave vessel at high temperatures. The autoclave was filled with deionized water and the samples, contained in the sample-holder, were placed in the vessel. The vessel was then pressurized by heating the contents in the vessel. The pressure valve on the vessel could release the excess water vapor (steam) in the vessel in order to stabilize the vessel at a required combination of temperature and pressure. The samples were held at a predetermined combination of temperature and pressure for a specific period of time before the vessel and its contents were cooled to room temperature.

The water that was used to pressurize the vessel was examined for traces of yttrium using Inductively Coupled Plasma (ICP) spectroscopy. The limit of detection for the ICP is a standard deviation of 0.0002 appm. ICP measurement of the water from each hydrothermal treatment showed no measurable traces of zirconium or yttrium.

Vickers hardness test was performed on the treated PYSZ samples. X-ray diffraction was used to identify the phases formed and quantify the amount of the monoclinic phase transformed from the tetragonal phase. Optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to observe macro-cracks, micro-cracks and regions on the surface that transformed from the tetragonal to the monoclinic phase. Kinetics of the phase transformation was determined by using the data on X-ray diffraction and statistical analysis of the measured thickness of the transformed layer.

3. Results and discussion

YPSZ samples were treated under hydrothermal conditions by exposing the samples in a pressurized autoclave at high temperature in the presence of water vapor. The treated samples were examined for mechanical property, surface morphology and the amount of the phases present after the treatment.

Surfaces of the treated and untreated samples were examined using an optical microscope. Fig. 1 shows a completely destroyed YPSZ sample after being treated at 200 °C at a vapor pressure of 10.34 MPa for 24 h. The hydrothermally treated sample showed macroscopic cracks on the surfaces. Fig. 2 shows the surface of an untreated sample that is devoid of surface cracks. Fig. 3 shows a large crack on a bulged surface of a hydrothermally treated sample. The bulge on the surface could have formed due to the volume expansion of the material that could have transformed from the tetragonal to the monoclinic phase which is normally accompanied by a 4% volume expansion. The amount and size of the cracks increased with the severity of the hydrothermal treatment. Samples treated at and above 200 °C at 10.34 MPa vapor pressure for 24 h or more lost mechanical integrity and failed catastrophically as shown in Fig. 1. Fig. 4 shows a cross-section of a sample that was treated hydrothemrally.

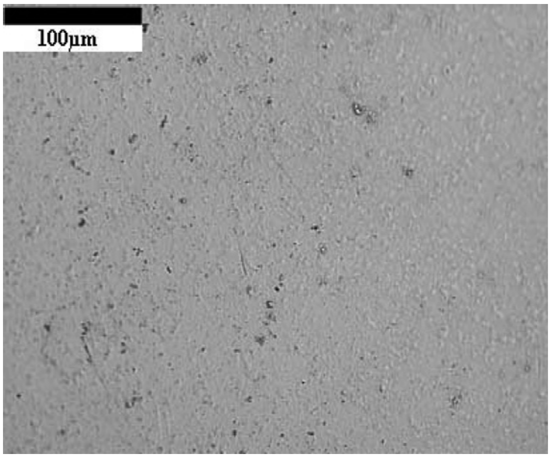

Fig. 2. Surface of an unexposed sample.

Observations from SEM micrographs of the untreated and the treated samples revealed morphological differences. Cracks were predominant features on the surface of the hydrothermally treated samples. The morphological differences of the surfaces as observed using an SEM are shown in Figs. 4 and 5. It is also observed that the cracks are intergranular in nature.

TEM micrographs showed the same pattern of cracks on the hydrothermally treated samples as the SEM micrographs. Fig. 6 shows a TEM micrograph of an untreated YPSZ sample. The inset in

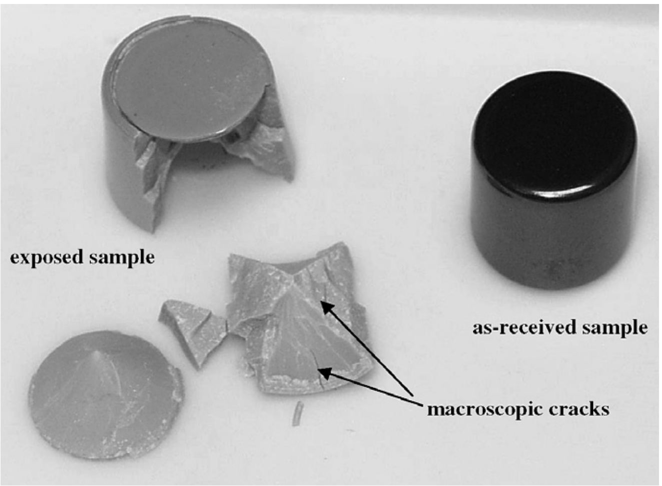

Fig. 1. YPSZ sample treated at 200 °C and water vapor pressure of 10.34 MPa for 24 h.

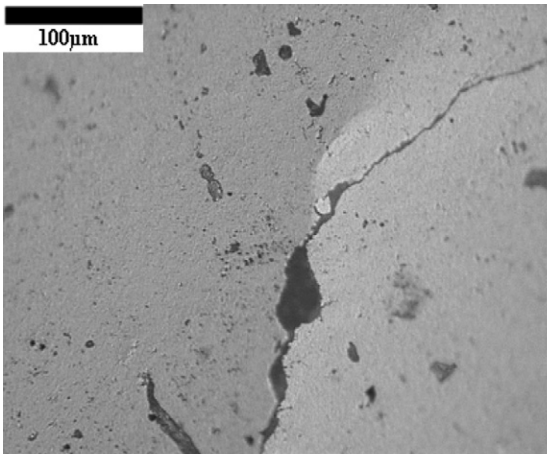

Fig. 3. Hydrothermally treated YPSZ sample having surface cracks. $T = 200$ °C, $P = 10.34$ MPa and $t = 24$ h.

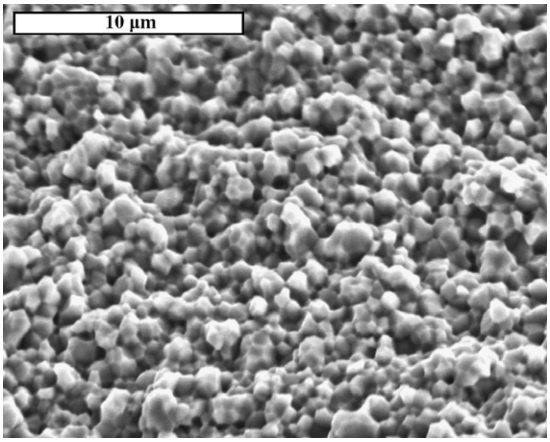

Fig. 4. SEM micrograph of an untreated YPSZ sample surface.

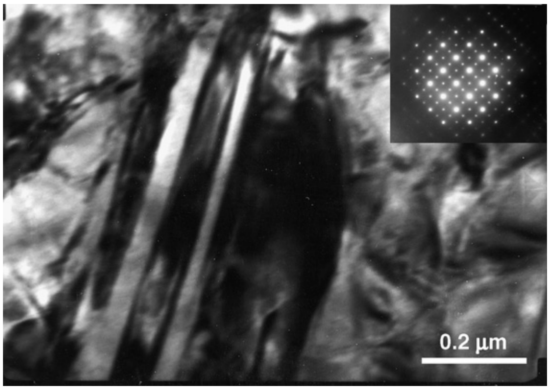

Fig. 6. TEM microstructure of an untreated YPSZ sample characterized as having a tetragonal crystal structure. The inset shows the SADP of the same region with *d*-spacing of 5.167 Å, $B = [001]$ and having a four fold symmetry.

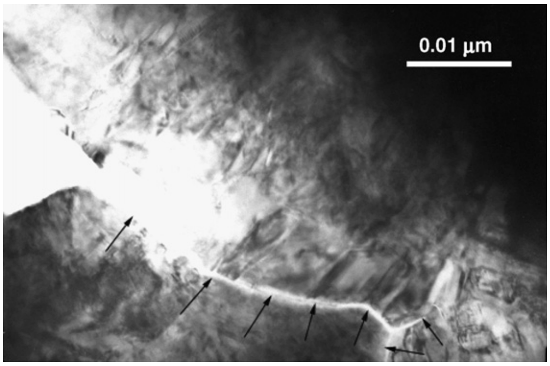

Fig. 7. TEM micrograph of YPSZ sample having micro cracks on the surface after being treated at 250 °C at 8.27 MPa for 12 h.

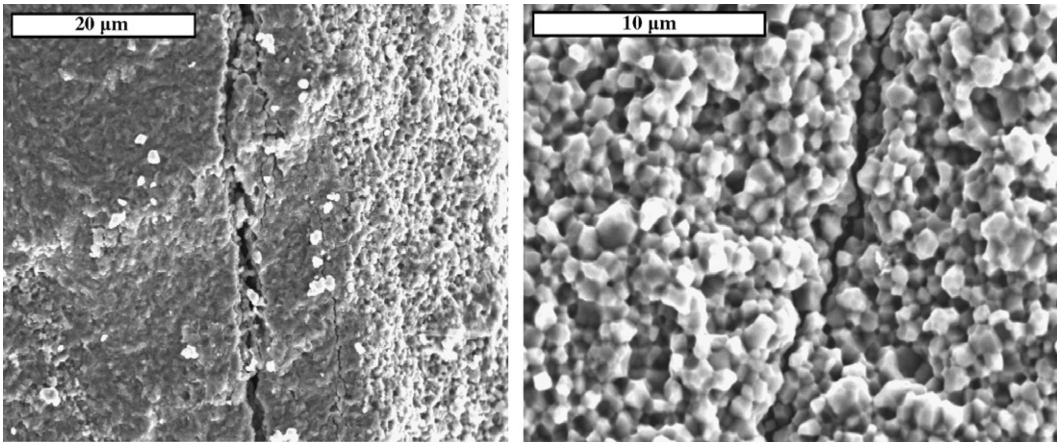

Fig. 5. SEM micrographs show surface cracks on the YPSZ sample treated at 250 °C at a water vapor pressure of 8.27 MPa for 12 h.

the figure is an electron diffraction pattern (SADP) of the area shown in the micrograph. The diffraction pattern shows a tetragonal crystal structure. The micrograph in Fig. 7 is representative of the nature of hydrothermally treated YPSZ samples. The sample in Fig. 7 was treated at 250 °C at 8.27 MPa for 12 h. The phase formed after hydrothermal treatment had monoclinic crystal structure.

X-ray diffraction patterns of the surface of hydrothermally treated samples were used to identify and quantify the phases prevalent on the surface of the samples [6]. The ratio of the intensities of the monoclinic and tetragonal peaks was used to quantify the amount of the tetragonal phase transformed to the monoclinic phase. The ratio of the sum of the intensities of the monoclinic $(\bar{1}\,1\,1)$ and $(1\,1\,1)$ reflections to the sum of the intensities of the monoclinic $(\bar{1}\,1\,1)$ and $(1\,1\,1)$ and tetragonal $(1\,1\,1)$ reflections was used to represent the fraction of the monoclinic phase present in the sample after the hydrothermal treatment. It is assumed here that the intensity of the tetragonal $(1\,1\,1)$ reflection is equal to the sum of the intensities of the monoclinic $(\bar{1}\,1\,1)$ and $(1\,1\,1)$ reflections as suggested by Garvie and Nicholson [7]. The assumption on which the linearity of the formula is based, is however, not strictly correct [7]. The method based on the intensity ratio is simple and enables the relative amount of the phases to be estimated easily where the ability to make the representative samples is difficult.

The intensity of reflection hkl, $H(hkl)$, in X-ray powder diffraction geometry, from the surface of a thick slab of crystal powder can be calculated as is explained by James [8], Azaroff [9] and Toraya et al. [10]. For the tetragonal → monoclinic phase transformation systems, the integrated intensity ratio X_{m} is defined by

$$X_{\mathrm{m}} = \frac{I_{\mathrm{m}}(\bar{1}\,1\,1) + I_{\mathrm{m}}(1\,1\,1)}{I_{\mathrm{m}}(\bar{1}\,1\,1) + I_{\mathrm{m}}(1\,1\,1) + I_{\mathrm{t}}(1\,1\,1)}, \tag{1}$$

where the subscripts m and t represent the monoclinic and tetragonal phases respectively.

The ratio X_{m} can be expressed as

$$X_{\mathrm{m}} = \frac{V_{\mathrm{m}}[H_{\mathrm{m}}(\bar{1}\,1\,1) + H_{\mathrm{m}}(1\,1\,1)]}{V_{\mathrm{m}}[H_{\mathrm{m}}(\bar{1}\,1\,1) + H_{\mathrm{m}}(1\,1\,1)] + (1 - V)H_{\mathrm{t}}(1\,1\,1)}, \tag{2}$$

where $H(hkl)$ is the intensity of reflection hkl, V_{m} is the volume fraction of monoclinic phase and that of the tetragonal phase is given by the $V_{\mathrm{t}} = 1 - V_{\mathrm{m}}$.

The untreated YPSZ samples have tetragonal crystal structure as seen in Fig. 8. Once the YPSZ sample is treated under hydrothermal conditions in an autoclave, some amount of the tetragonal YPSZ transforms to the monoclinic phase. Fig. 8 compares the X-ray patterns of an untreated sample with a sample hydrothermally treated to 200 °C at a vapor pressure of 2.07 MPa for 12 h. The $(1\,1\,1)_{\mathrm{t}}$ peak of the tetragonal phase and the $(\bar{1}\,1\,1)_{\mathrm{m}}$ and $(1\,1\,1)_{\mathrm{m}}$ peaks of the monoclinic phase are compared to estimate the relative amounts of the two phases. It is observed in Fig. 8 that the $(1\,1\,1)_{\mathrm{t}}$ peak splits to form the $(\bar{1}\,1\,1)_{\mathrm{m}}$ and the $(1\,1\,1)_{\mathrm{m}}$ peaks after the sample has been hydrothermally treated. This

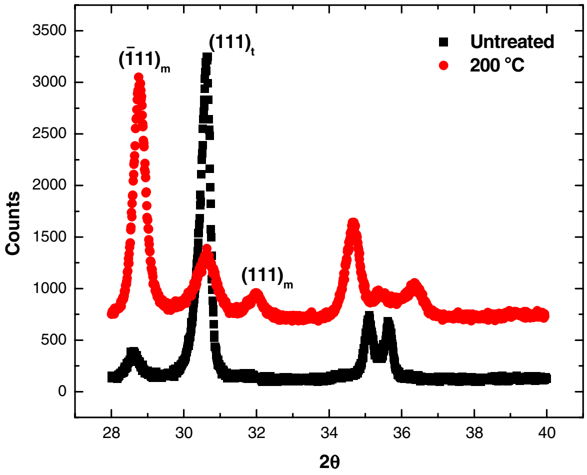

Fig. 8. X-ray diffraction patterns of an untreated YPSZ sample and a sample treated at $T = 200$ °C, $P = 2.07$ MPa for 12 h.

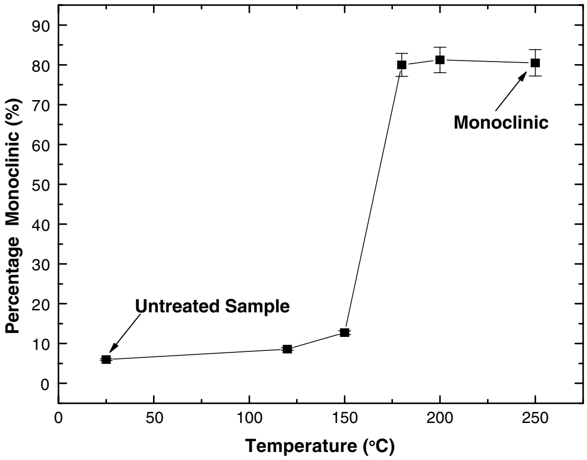

Fig. 9. Percentage of the monoclinic phase versus temperature of exposure after YPSZ samples were samples exposed for 12 h.

indicates that the tetragonal YPSZ has partially been transformed to monoclinic YPSZ during the hydrothermal treatment. The extent of the transformation depends on the temperature (Fig. 9) and period of exposure (Fig. 10). Fig. 11 shows the X-ray diffraction patterns of the three samples hydrothermally treated at 100 °C, 120 °C and 150 °C at a pressure of 0.69 MPa for 12 h. It was observed that the $(\bar{1}\,1\,1)_m$ peak becomes more prominent at the expense of the $(1\,1\,1)_t$ peak as the temperature of exposure increased from 100 °C to 150 °C as seen in Fig. 11.

The mechanical properties of the YPSZ samples were affected by the transformation from the tetragonal to the monoclinic phase after the hydrothermal treatment of the YPSZ samples. Surface hardness of the treated samples was measured using the Vickers indenter. Fig. 12 shows that the hardness of the YPSZ samples decreased with increasing amounts of the monoclinic phase. Mechanical properties like hardness deteriorate with the severity of the hydrothermal treatment.

The outer transformed layer could be distinctly identified from the inner untransformed material using an optical microscope as shown in Fig. 13. Thickness of the transformed layer was measured for different periods of exposure under similar hydrothermal conditions as shown in Fig. 10. The thickness of the transformed layer increased with

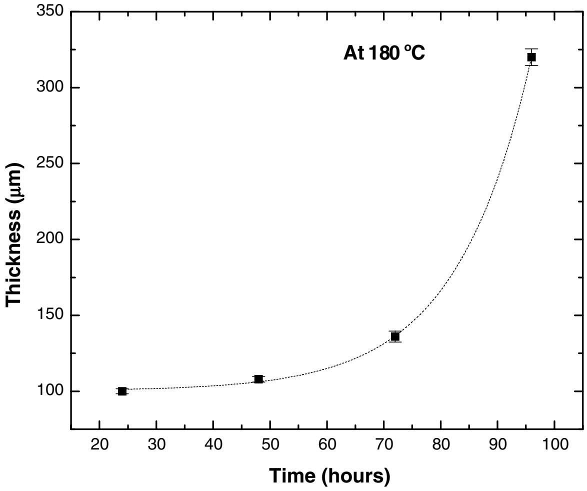

Fig. 10. Thickness of transformed layer versus time of exposure.

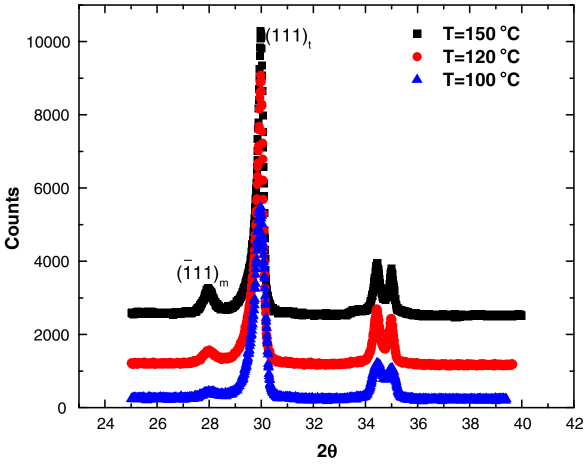

Fig. 11. X-ray diffraction patterns of YPSZ samples treated at 100 °C, 120 °C and 150 °C at pressure less than or equal to 0.69 MPa for 12 h.

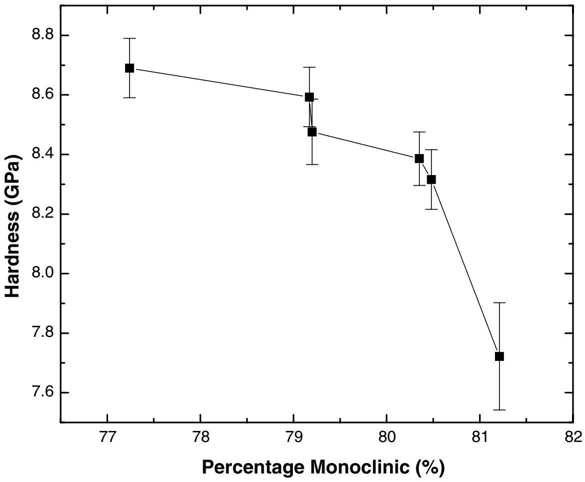

Fig. 12. Hardness of the hydrothermally exposed YPSZ sample surface versus the percentage monoclinic content.

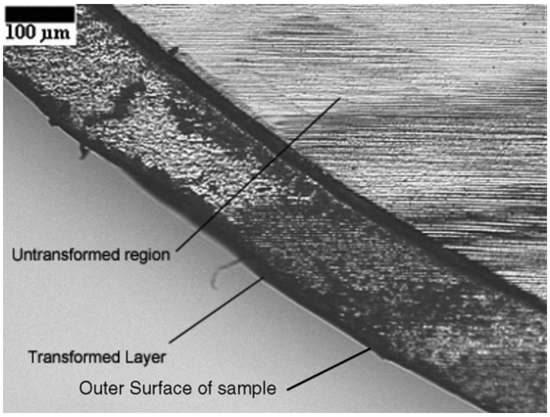

Fig. 13. Cross section of a YPSZ sample treated at 200 °C at a pressure of 2.07 MPa for 12 h.

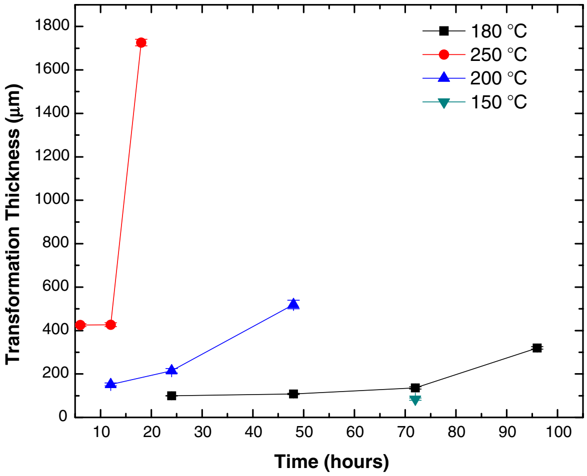

Fig. 14. Variation of thickness of the transformed layer with time for hydrothermal treatments with varied temperatures.

the duration of the hydrothermal treatment. Fig. 10 shows that the points plotted fitted well with an exponential growth curve and could be represented by the equation

$$x = A + B\exp(kt), \tag{3}$$

where A, B and k are constants. x is the thickness of the transformed layer and t = duration of the hydrothermal treatment. Fig. 14 shows the variation of the thickness of the transformed layer with the duration of the hydrothermal treatment for varied temperature conditions.

The transformation process could be rate limited by various factors. Diffusion of water into the interior of the bulk or nucleation of the monoclinic phase could be rate-limiting factors that could affect the kinetics of phase transformation.

4. Conclusion

YPSZ transforms from tetragonal to monoclinic phase when exposed to elevated temperatures in the presence of water or water vapor. Mechanical properties are affected due to the transformation to the monoclinic phase. The amount of the tetragonal phase transformed to the monoclinic phase by the hydrothermal treatment is proportional to the temperature and duration of the treatment.

References

[1] D.J. Green, R.H.J. Hannink, M.V. Swain, Transformation Toughening of Ceramics, CRC Press, Boca Raton, FL, 1989, 5.
[2] C.J. Howard, R.J. Hill, B.E. Reichert, Acta Crystallogr. B44 (1988) 116.
[3] R.C. Garvie, R.H.J. Hannink, R.T. Pascoe, Nature 258 (5537) (1975) 703.
[4] I-Wei Chen, J. Am. Ceram. Soc. 74 (10) (1991) 2564.
[5] M.G. Scott, J. Mater. Sci. 10 (1975) 1527.
[6] E.D. Whitney, Trans. Faraday Soc. 61 (9) (1965) 1991.
[7] R.C. Garvie, P.S. Nicholson, J. Am. Ceram. Soc. 55 (6) (1972) 303.
[8] R.W. James, Optical Principles of the Diffraction of X-rays, The Crystalline State, 2, G. Bell and Sons, London, 1967, p. 34.
[9] L.V. Azaroff, Acta Crystallogr. 8 (7–12) (1955) 701.
[10] H. Toraya, M. Yoshimura, S. Somiya, Communications of the American Ceramic Society (June) (1984) C119.