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Corrosion of yttria-fully stabilized zirconias in molten fluorides

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Yttria-fully stabilized zirconia ceramics were manufactured from home-made and commercially available powders and were sintered under different conditions. The ceramics were immersed in the corrosive environment of molten LiF, NaF, KF (FLINAK) eutectic for up to 360 h from 700–900 °C. The changes caused in the crystal structure were probed with laser Raman spectroscopy and X-ray diffraction. The degree of corrosion (phase transformation) depends on immersion period, FLINAK temperature, and ceramics microstructure. From the tested ceramics, ZrO_2–8 mol % Y_2O_3 with a grain size larger than 8 μm and having zero open porosity, exhibits the best resistance to the corrosive influence of FLINAK.

1. Introduction

Certain ceramics are used as containers of molten salts and as sensors in molten salt baths. The endurance of these materials in such environments depends both on the reactivity as well on changes caused by fused salts on the crystal structure which, in turn, reflects a change in properties such as mechanical strength and ionic conductivity.

The crystal structure of zirconia, one of the best corrosion-resistant and refractory materials, is known to change from monoclinic to tetragonal and then to cubic at 1150 and 2200 °C, respectively [1,2]. By adding heterovalent cations, such as Mg^{2+}, Ca^{2+}, Y^{3+}, to pure zirconia the tetragonal and cubic forms remain stable even at room temperature [3,4]. The stabilization process itself is due to the formation of oxygen vacancies to preserve the charge equilibrium. The mobile defects, in turn, are responsible for the high conductivity [5] of these materials, a property which has found several applications such as in oxygen control devices [6]. Stabilized zirconia systems have improved mechanical properties with respect to fracture strength and resistance to thermal shock [7].

Although much work has already been published on fully stabilized yttria-doped zirconias (Y-FSZ), which are the most widely used doped zirconia, its stability in molten fluorides and the parameters effecting it have not been examined. In this work, Y-FSZ was prepared from home-made and commercially available powders and was sintered under different conditions. The doped zirconias were immersed in molten FLINAK and the changes (corrosion) caused on their crystal structure, i.e. transformation of the cubic phase to monoclinic, were evaluated. The results were used to assess the influence of the different parameters, such as grain size or salt bath temperature, on the ceramic's stability in such a hostile environment. The techniques used for the estimation of the degree of corrosion were X-ray diffraction (XRD) and laser Raman spectroscopy (LRS).

Although LRS has been used in the past to study the transitions of pure and stabilized zirconia systems during heating and cooling cycles [8–13] this is the first time, to our knowledge, that it has been used as a quantitative tool to estimate the degree of corrosion caused by molten fluorides.

2. Experimental procedure

2.1. Sample preparation

Y-FSZ powders (containing 8 mol % Y_2O_3) either commercially available or chemically prepared (coprecipitation method) were utilized for sample preparation. The commercial powders used were either already stabilized (purchased from Zirconia Sales or Tosoh) or pure monoclinic zirconia powders (Unitec) which were stabilized with yttria (Alfa Products).

For the yttria stabilization, monoclinic zirconia was mixed with the appropriate quantity of stabilizer and the mixture was ball-milled using zirconia grinding media. The particle-size distribution of the powders was regularly measured and milling continued until no significant change was observed between two measurements.

Chemical powders of yttria-fully stabilized zirconia were also produced through coprecipitation. High-purity salts of $ZrOCl_2 \cdot 4H_2O$ and $YCl_3 \cdot 6H_2O$, in the appropriate quantities, were diluted in distilled water (0.25 M total concentration). The resulting solution

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TABLE I Method of preparation and microstructure of Y-FSZ ceramics[a]

Powders origin	Method of formulation	Firing conditions (°C)	(h)	Microstructure	Density (g cm^{-3})
Zirconia Sales	Cold isostatic pressing	1700	2	Grain size 30 μm, no closed porosity	5.94
		1600	2	Grain size 8 μm, no closed porosity	5.93
		1600	0	–	5.90
		1500	5	Amorphous surface	5.88
		1500	2	Grain size 3–6 μm, closed porosity < 0.5%	5.90
		1400	5	Grain size 1–3 μm, closed porosity < 1%	5.93
		1400	2	Grain size 1–2 μm, closed porosity < 1%	5.87
Cereco[b]	Cold isostatic pressing	1600	2	Grain size 1–2 μm, closed porosity	5.31
		1600	0	–	6.0
Coprecipitated	Cold isostatic	1600	2	–	5.50
powder	pressing	1600	5	–	5.80
Zirconia Sales 94%, coprecipitated powder 6%	Cold isostatic pressing	1550	2	Amorphous surface + grains of size 1 μm, no closed porosity	
Zirconia Sales 88%, coprecipitated powder 12%	Cold isostatic pressing	1550	2	Amorphous surface, no closed porosity	
Zirconia Sales	Slip casting	1600	2	Grain size 2–3 μm	5.90
		1500	5	Grain size 2 μm	5.87
		1500	2	Grain size 2 μm	5.88
		1400	5	Grain size 1 μm	5.91
		1400	2	Grain size 1 μm	5.86

[a] Referred to ZrO_2 8 mol % Y_2O_3 ceramics.
[b] Powder is produced by doping monoclinic zirconia (Unitec) with yttria (8% mol).
[c] This sample exhibits 15% open porosity. Open porosity of all other samples is very close to zero.

was added dropwise to a vigorously stirred 3.2 M NH_3 solution of such a volume that the final concentration of the zirconium and yttrium hydroxide was 0.125 M. The pH was always maintained above 10, to ensure complete reaction and a white, gelatinous precipitate was produced.

The resulting gel was washed twice with distilled water and the residual chlorine in the wash effluent was qualitatively determined by adding a few drops of a $AgNO_3$ solution. The gel was washed a further three times with 100% ethanol and the remaining liquid was removed by centrifuging after each wash. Drying (at 60 °C for 24 h and at 110 °C for a further 24 h) and dry grinding for 1 h followed.

A combination of thermo gravimetric and differential thermal analysis (TG-DTA) with X-ray diffraction analysis was employed to determine the crystallization temperature, whilst dilatometric measurements were performed to investigate the densification rate.

Cold isostatic pressing (300 MPa) was used for preparing the samples, while some specimens were also prepared using the slip-casting shaping technique.

The compacts were sintered in open air for 2–5 h at temperatures ranging from 1400–1700 °C. The sintered specimens were in the form of cubes (1 cm × 1 cm × 1 cm). The external surfaces of the samples were polished (with grinding paper 400 mesh) in order to achieve uniform surface furnish.

2.2. Characterization of ceramics

All the samples were characterized before and after the FLINAK test. Porosity and pore-size distribution measurements were performed by mercury porosimetry (Quantachrome A-33).

Density measurements were made by geometrical volume determination, Archimedes' principle or porosimeter data. X-ray diffraction analysis (Siemens D-500 diffractometer, CuK_α radiation) was used to detect the crystalline phases present and the extent of the phase transformations.

Scanning electron microscopy studies were also carried out in order to investigate the morphology of the ceramic's surface before and after the treatment with FLINAK. All the ceramics manufactured, as well as the origin of the powders, firing conditions and physical characteristics (density, microstructure), are summarized in Table I.

2.3. Corrosion tests

Fluoride salts were purchased from Merck (p.a. grade) and were purified further by melt crystallization. FLINAK was prepared by mixing the recrystallized compounds in a glove box. A home-made oven with three heating zones and programmable heating controller and two programmable Scandiaonven furnaces were used. All furnaces were equipped with a nickel tube core and were modified in order to accommodate the need for vacuum and/or inert atmosphere. Each of the ceramics was immersed in 50 g molten FLINAK for a maximum of 360 h and at temperatures up to 900 °C under an argon atmosphere. Vitreous carbon crucibles (Le Carbone, Lorraine) were chosen as containers for the FLINAK. The solidified FLINAK was removed mechanically after submerging the samples in water for 48 h.

2.4. Identification of phases

Two techniques were used to evaluate the degree of corrosion, XRD and LRS.

2.4.1. X-ray diffraction

XRD analysis was used to identify phase transformations due to corrosion. Estimation of the corrosion depth was also made by performing XRD measurements of the surface of some corroded samples after the removal of successive layers by grinding (Fig. 1).

An estimation of the relative quantity of cubic phase present at different depths was made using the intensity of the peaks of cubic (I_c (1 1 1)) and monoclinic (I_m ($\bar{1}$ 1 1)) phases and calculating the ratio

$$R_x = \frac{I_c(1\,1\,1)}{I_c(1\,1\,1) + I_m(\bar{1}\,1\,1)} \tag{1}$$

2.4.2. LRS

The quantitative use of LRS for the cubic-to-monoclinic transformation was based on the measured intensities of the 617 and the 476 cm^{-1} bands [14] (Fig. 2). The intensity of the 617 cm^{-1} band, I^{617}, is attributed to overlap the cubic phase broad band (Fig. 2a) with a monoclinic phase peak. The band at 476 cm^{-1} is characteristic of the monoclinic phase, and its intensity was measured by excluding the peak "background" level, which is a property of the cubic phase (Fig. 2a). Before any measurement was made, the intensity at 800 cm^{-1} was subtracted from each spectrum [14]. In order to obtain the monoclinic phase molar fraction in the corroded ceramics, the intensities, calculated as described above, were introduced into the following equation [14]

$$x_m = \frac{I_m^{476}0.12}{I^{617} - I_m^{476}0.29} \tag{2}$$

where x_m is the monoclinic phase molar fraction.

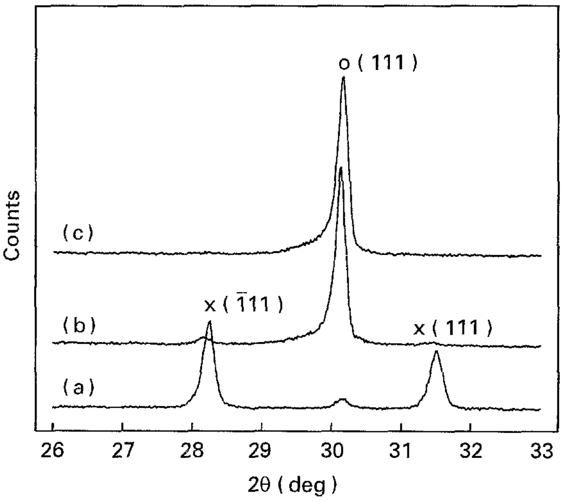

Figure 1 XRD analysis of Y-FSZ, demonstrating the (O) cubic to (×) monoclinic transformation, after immersion in FLINAK at 700 °C for 20 h, (a) at the sample surface, (b) at 35 μm depth, (c) at 45 μm depth; samples were prepared from "Zirconia Sales" powder and fired at 1600 °C for 2 h (cold isostatically pressed samples).

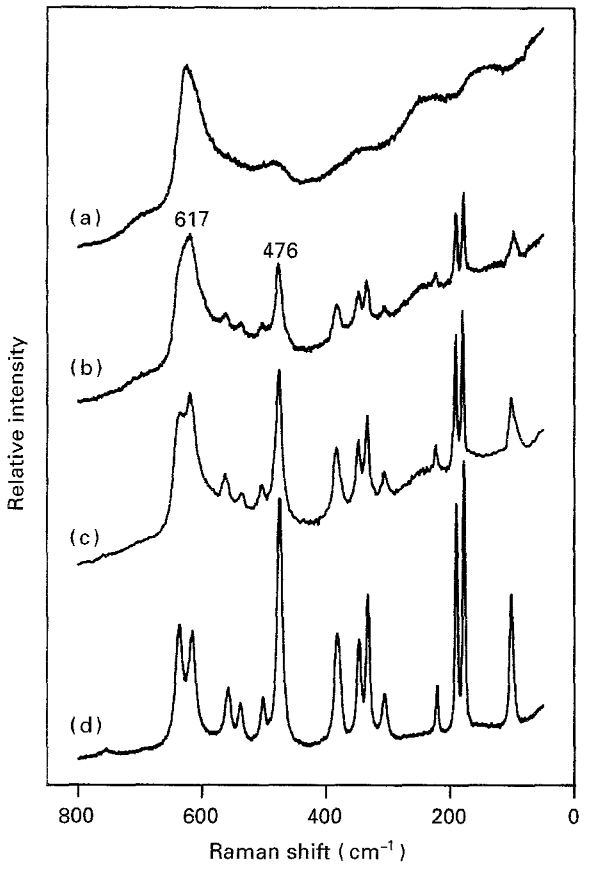

Figure 2 Raman spectra of ZrO_2–8 % mol Y_2O_3 ceramics, demonstrating the cubic to monoclinic transformation, after immersion in FLINAK at 700 °C for (a) 0 h (cubic phase), (b) 5 h, (c) 20 h and (d) 150 h; samples were prepared from "Zirconia Sales" powder and fired at 1700 °C for 2 h.

Raman spectra were excited with the 488 nm line of a 4 W Spectra Physics argon laser. The plasma lines were removed from the laser beam by using a small monochromator as filter. A cylindrical lens, with 127 mm focal length, was used to focus the laser line on the sample giving a probed area of approximately 1 mm^2. The scattered light was collected at an angle of 90° and analysed with a SPEX 1403, 0.85-m double monochromator equipped with a −20 °C cooled RCA photomultiplier and EG&G/ORTEC electronic amplifier using photon-counting. The power of the incident laser beam was about 100 mW distributed over the surface of the sample. The typical spectral width and time constant were 1 cm^{-1} and 3 s, respectively. The system was interfaced with a computer, and spectra were recorded.

3. Results and discussion

3.1. Corrosion dependence on immersion time

XRD analysis as well as the Raman spectra excited from sample surfaces, after their immersion into FLINAK at 700 °C for different periods of time (Table II), indicate that (a) corrosion depends strongly on immersion time (Fig. 2), and (b) the presence of the monoclinic phase is observable even after only 5 h in FLINAK at 700 °C.

From the data of Table II the corrosion rates can be calculated if the following assumptions are made: (a) the only kinetically active components are F^- and Y^{3+}, (b) the concentration of F^- remains nearly constant, (c) the F^- reacts with the dopant by entering the oxygen vacancies of the cubic phase crystal structure. Because two Y^{3+} are needed for the creation of one oxygen vacancy, the reaction can be described as pseudo-second-order of a single component (Y^{3+}). The relationship describing such a reaction is given by [15]

$$x_c^{-1} = kt + x_{c0}^{-1} \quad (3)$$

where x_c is cubic phase molar fraction, x_{c0} the cubic phase molar fraction before the corrosion, t is the immersion time in the FLINAK and k is the corrosion rate constant representing the conversion of cubic phase molar fraction in the unit of time. From the plot of x_c^{-1} versus time (Fig. 3) k was found to be equal to $8.3 \times 10^{-3}\ h^{-1}$ and $1.03 \times 10^{-2}\ h^{-1}$ for the ceramics fired at 1700 °C for 2 h and at 1400 °C for 5 h, respectively.

The depth at which corrosion is evident (transformation of the cubic phase to monoclinic) depends also on immersion time, as can be seen in Table III.

3.2. Corrosion dependence on FLINAK temperature

Application of LRS on ceramics immersed for 15 h in FLINAK at 700, 800 and 900 °C indicates that corrosion depends strongly on FLINAK temperature (Table IV). The ceramics fired at 1700 °C display better resistance than those fired at 1400 °C, even at higher temperatures. Corrosion depth depends also on FLINAK temperature. The drastic influence can be seen in Table V where a 100 °C difference in the temperature of the molten bath can practically double the corrosion depth.

3.3. Corrosion dependence on microstructure

SEM studies (Table I) on samples sintered under various firing conditions before and after corrosion showed (in agreement with XRD and LRS results) that all samples are affected by the molten fluorides, and their microstructure has been changed (Fig. 4) after corrosion. The microstructure before corrosion is characterized by the presence of grains of uniform size (affected by the firing schedule) and occasionally the presence of an amorphous phase (high firing temperature, long sintering time or coprecipitated powder).

TABLE II Corrosion dependence of ceramic[a] on immersion time

Sintering conditions (°C)	(h)	Time in FLINAK[b] (h)	Monoclinic molar fraction[c]
1400	5	5	0.05
1400	5	15	0.14
1400	5	100	0.49
1700	2	5	0.04
1700	2	15	0.11
1700	2	20	0.14
1700	2	150	0.55

[a] Referred to ZrO_2 8 mol % Y_2O_3 ceramics prepared from "Zirconia Sales" powder.

[b] FLINAK temperature was 700 °C.

[c] The monoclinic phase molar fraction was measured at the sample surface after treatment using LRS.

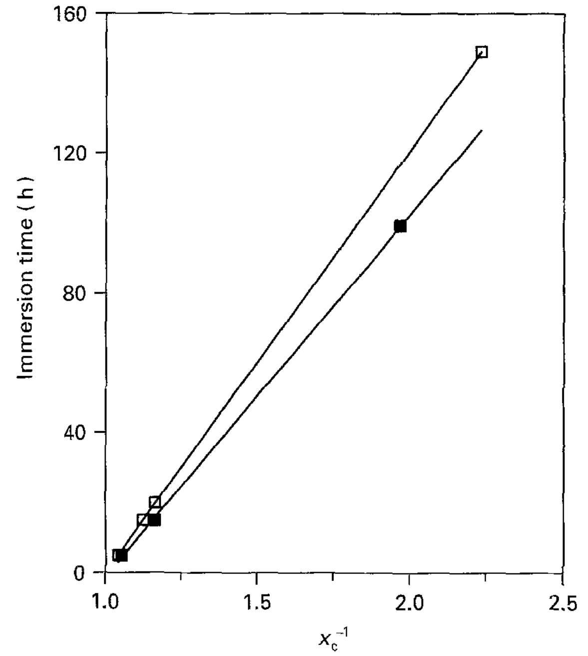

Figure 3 Immersion time in FLINAK versus the inverse cubic phase molar fraction. The ceramics were fired at (■) 1700 °C for 2 h and (□) 1400 °C for 5 h.

TABLE III Dependence of corrosion depth of ceramic[a] on grain size

Sintering conditions (°C)	(h)	Grains (μm)	Corrosion depth[b] (μm) After immersion in FLINAK 5 h	15 h	100 h	150 h
1400	2	1–2	35	60		
1400	5	1–3	35	60		
1500	2	3–6	–	55		
1500	5	Amorphous	–	35	140	180
1600	2	8	–	30	120	150
1700	2	30	15	–		

[a] Referred to ZrO_2 8 mol % Y_2O_3 ceramics prepared from "Zirconia Sales" powder by cold isostatic pressing (300 MPa). Bath temperature 700 °C.

[b] Referred to the minimum distance from the external surface of a ceramic at which no monoclinic phase exists. Phase percentage was measured using X-ray diffraction.

TABLE IV Corrosion dependence of ceramic[a] on FLINAK temperature

Sintering conditions (°C)	(h)	FLINAK temperature[b] (°C)	Monoclinic molar fraction[c]
1400	5	700	0.14
1400	5	800	0.55
1400	5	900	0.90
1700	2	700	0.11
1700	2	800	0.48
1700	2	900	0.70

[a] Referred to ZrO_2 8 mol % Y_2O_3 ceramics prepared from "Zirconia Sales" powder.

[b] Immersion time was 15 h.

[c] The monoclinic phase molar fraction was measured at samples' surface after the treatment by using LRS.

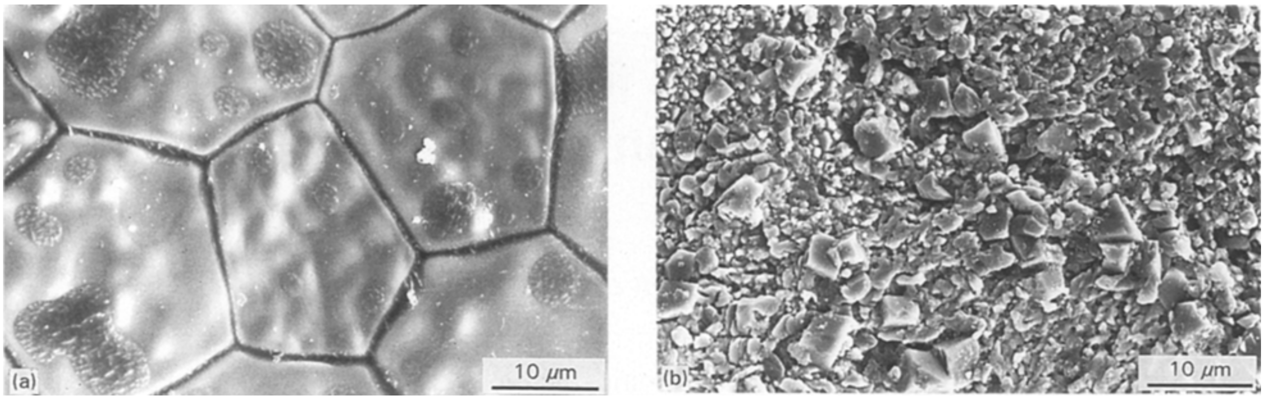

Figure 4 Micrograph of an Y-FSZ prepared from "Zirconia Sales" powder and sintered at 1700 °C for 2 h (cold isostatically pressed samples), (a) before and (b) after FLINAK treatment.

TABLE V Dependence of corrosion depth of ceramic[a] on FLINAK temperature

Depth (μm)	FLINAK temperature[b] (°C)	R_x[c]
150	800	0.84
250	800	0.91
370	800	0.94
250	900	0.76
400	900	0.83

[a] Referred to ZrO_2 8 mol % Y_2O_3 ceramics prepared from "Zirconia Sales" powder and sintered at 1700 °C for 2 h.

[b] Immersion time was 15 h.

[c] $R_x = I_c(1\,1\,1)/[I_c(1\,1\,1) + I_m(\bar{1}\,1\,1)]$, where $I_c(1\,1\,1)$ and $I_m(\bar{1}\,1\,1)$ are the X-ray diffraction intensities of the (1 1 1) cubic and ($\bar{1}$ 1 1) monoclinic peaks, respectively.

After corrosion, all the samples exhibit almost the same microstructure which is characterized by grains of 1–2 μm size.

The corrosion depth under various corrosion conditions of all these samples was also studied. It was found that even at short corrosion times the outer surface was affected. Depletion of the stabilizing oxide caused the cubic phase to transform into monoclinic zirconia. However, the depth at which corrosion is evident depends on physical properties (open porosity) and ceramics microstructure (Table III). Corrosion resistance is maximized when no amorphous phase is present, while the grain size is uniform and larger than about 8 μm. Such a microstructure can be achieved when samples from conventional powders are fired at up to 1600–1700 °C for 2 h.

Y-FSZ powders prepared following chemical routes (coprecipitation) were used to prepare samples that were corrosion tested, but no significant improvement in corrosion behaviour was observed.

Zirconia ceramics made from a mixture of conventional with chemical powders were characterized by a non-uniform grain size (Table 1). When corrosion tested, these ceramics showed no improvement compared to ceramics prepared from conventional powders.

Samples prepared by the slip-casting technique and sintered at the same conditions as the isostatic samples, exhibited a lower corrosion resistance than the latter. This can be attributed to their finer microstructure (Table I).

4. Conclusion

The endurance of the Y-FSZ in molten fluorides depends on (a) the bath temperature, where a 100 °C difference in temperature results in changing the corrosion depth by a factor of 2, (b) the immersion time in FLINAK, which is linearly related to corrosion rate, and (c) the microstructure and consequently sintering conditions. The optimum grain size diameter was found to be larger than about 8 μm.

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