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Original article

A combined structural, microstructural and dilatometric analysis of MgPSZ

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ABSTRACT

MgO-doped partially stabilized zirconia (MgPSZ) is a ceramic where three phases (cubic, tetragonal and monoclinic zirconia) might coexist due to non-equilibrium conditions and proper quantification of phase content is difficult. Here, a few selected compositions (in the 7–10 mol% MgO range) and firing profiles were studied in order to cover several phase compositions and microstructural features. An original attempt is made to correlate data obtained by X-ray diffraction (XRD), dilatometry (DIL) and scanning electron microscopy (SEM). Distinct software packages used in the analysis of XRD patterns of different samples confirmed the shortcomings of the assessment of phase content in sintered bodies while proper handling of DIL data provided complementary quantitative information on their phase content. The suggested procedure can be further used to obtain a subtle insight on phase development with temperature, subject of major relevance with respect to tuning of the mechano-thermal behavior of these ceramics.

1. Introduction

Zirconia-based materials are popular ceramics used for many years in mechanical, thermal and electrochemical applications [1–3]. More recently several compositions were also considered as biomaterials [4]. However, pure zirconia is of little use due to a series of phase transformations with temperature, one of them (M-Monoclinic ↔ T-Tetragonal) with a large volume change, often source of mechanical failure of sintered bodies.

Doping of zirconia is the adopted solution to enlarge the stability domain of the cubic (C-Cubic) and/or T phases. Besides composition, microstructure can also be adjusted to obtain the so-called partially stabilized zirconias (PSZ) where the C and T phases prevail. These materials are known for their toughness, being named as ceramic steel after their discovery. The expansive T → M phase change has a main role in this behavior, preventing or deflecting the progression of crack tips [5–12].

In binary systems including alkaline-earth oxides (e.g., MgO or CaO) there is a wide C phase field at high temperature for significant dopant levels [13–15]. However, in normal PSZ materials the exploited compositional range corresponds to coexisting C and T phases at sintering temperatures. These phases are unstable at low temperature, when the M phase should prevail. This apparent stability drawback is used to manipulate phase composition and microstructure in manners similar to artificial ageing in metal alloys, originating materials with impressive thermal shock resistance. These materials are widely used in oxygen sensors for molten metals where thermal shock resistance is crucial [16–22].

In the case of MgO doped PSZ (MgPSZ), usual phase diagrams indicate that the solubility of MgO either in the M or the T phases is small (< 1.5 mol%) while reports on the eutectoid composition and temperature (C → T + MgO) pinpoint close values (13–14.8 mol% and 1400–1420 °C, respectively). The same is true for the T → M phase transition temperature (1120–1240 °C) [14,15]. These values are mentioned here since they will be used as guidance to define boundaries for the analysis of dilatometric data.

The structural analysis of MgPSZ always faced several problems, either using X-ray diffraction (XRD) or Raman spectroscopy [8,23–26]. Firstly, in XRD patterns there is a considerable vicinity between the main peaks of the C and T phases, preventing a simple peak deconvolution. Secondly, analysis of powders is not representative of sintered samples since the T → M phase transition is easily triggered on milling. In fact, analysis of powders is considered the most reliable solution to assess the exact C phase content since the phase composition moves from M + T + C to M + C on milling.

The separate assessment of the M and the C + T phase content is

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considered quite effective with sintered samples. However, analysis of sintered samples must take into consideration that phase composition might change with the sample thickness since T grains in the interior of the sample are often constrained (unable to expand to M) while those at the surface can easily convert into M [12]. As summary, MgPSZ are complex ceramic electrolytes where the C, T and M phases might co-exist and their quantification using standard XRD is not easy.

Dilatometry is a characterization technique used frequently to assess thermal expansion coefficients or monitor dimensional changes during sintering. However, in the field of steel alloys (facing transformations with significant volume changes) this tool is also quite often exploited to try to quantify phase contents [27–30]. To our knowledge this type of scrutiny was never attempted with MgPSZ, irrespective of the mentioned drawbacks of standard phase quantification methods. The present work will address this possibility using a few MgPSZ compositions and firing conditions for this purpose. The procedure relies on several assumptions on the dependence of phase composition on temperature, also adequate mass and volume balances, duly detailed in the following sections.

2. Experimental

Materials prepared in this work were obtained after ball milling of high purity (> 99 wt%) MgO and ZrO_2 as precursors. HfO_2 was the major secondary oxide present (in the 1 wt% range in the ZrO_2 precursor). The prepared compositions were in the 7–10 mol% MgO range. This range of compositions is often used in oxygen sensor technology with the upper limit exploiting already the vicinity of the single C phase field at peak sintering temperatures [14]. The adopted acronym for these compositions will be xMgPSZ where x indicates the MgO mol% content (e.g., 7MgPSZ = ZrO_2 + 7 mol% MgO). Samples, shaped as disks or bars, were obtained using uniaxial pressing (130 MPa) before firing at 1700 °C for 3 h. Cooling rates in the 1 to 2 °C min^{-1} range complemented the peak sintering temperature plateau. MgPSZ tubes from an industrial supplier and produced using proprietary conditions were also tested.

XRD was used to inspect sintered and powder samples, using distinct setups (Panalytical Empyrean and X´Pert Pro3) and software packages (GSAS, Fullprof and Highscore), to test the robustness of phase analysis. The adopted fitting procedure in each case is shortly detailed below.

One first set of analyses involved the three distinct software packages but the same source data files obtained for distinct sintered samples. One single setup using (CuKα > X-radiation) with a Ni filter, a linear PIXEL detector fixed divergence slit of 1/2°, and a spinner sample holder, in a Bragg–Brentano para-focusing optics configuration. Intensity data were collected by the continuous counting method (step 0.02° and time 200 s) in the 20–90° 2θ range. Distinct (narrower) 2θ ranges were also considered, yielding roughly the same results when only the 23–67° 2θ range was adopted. Only the latter sets of results will be presented here.

In the analysis of powder patterns (obtained milling the sintered samples) an even narrower 2θ range (23–37°) was found enough to provide consistent sets of data, as discussed later in this work. This range includes the main C and M peaks, often adopted for phase quantification in these systems [8].

A few XRD patterns involving previously sintered 7.5MgPSZ samples (cooled from the sintering temperature at 2 °C min^{-1}) were also performed in the 26–33° 2θ range with constant heating rate (10 °C min^{-1}), from 500 to 1400 °C. This narrow 2θ range was adopted to try to ensure a heating profile similar to the conditions used in dilatometry.

The Rietveld method [31], as implemented in the GSAS software package [32] – using its EXPGUI graphical interface [33] – was used in the quantitative phase analysis (QPA) of the studied materials. The starting atomic parameters for M, T and C-ZrO_2 polymorphs were taken from the literature [24]. QPA analyses were performed refining the following parameters: scale-factors and zero-point, eight coefficients of the shifted Chebyshev function to fit the background, unit cell parameters, and the profile was modelled using the Thompson-Cox-Hasting formulation of the pseudo-Voigt function [34] refining one angle-independent Gaussian term (G_W), and two Lorentzian terms (L_X and L_Y); peak correction for asymmetry effects and specimen displacement were also refined.

The QPA and pattern fitting also used the FullProf suite as alternative [35]. The final profile analysis refinement involved the following profile parameters: one scale factor, three half-width (a Pseudo-Voigt peak shape function was used), seven cell parameters for the three phases, two peak asymmetry parameters; global, one zero point, six coefficients of polynomial background.

The profile analysis refinement using Highscore involved the following parameters: structural; one overall isotropic temperature factor; profile, one scale factor, three half-width (a Pseudo-Voigt peak shape function was used), cell parameters, no asymmetry parameters; global, one displacement point, three coefficients of polynomial background.

The structure values used for refinement either using FullProf or Highscore were extracted from references ICDD 04-001-9307, 04-012-8132 and 04-013-4343 (mean values with high quality and structure data). Examples of previous own work on structural characterization using distinct software packages in QPA are well documented [36–38].

As evidenced in the following section, all analyses of phase content with milled powders were equally effective. This is the crucial information for the adopted procedure where structural and dilatometric data are combined to yield information on phase content of sintered bodies. Accordingly, phase quantification involving distinct compositions (7.5 and 10 MgPSZ) and cooling rates (1 or 2 °C min^{-1}) was obtained using exclusively one software package (Fullprof). This selection was based solely on practical considerations outside the scope of this work.

Sintered samples were also inspected by scanning electron microscopy (SEM, Hitachi SU-70) equipped with energy dispersive spectroscopy (EDS, Bruker QUANTAX 400). After discarding distinct preparation procedures (thermal etching for inducing phase changes during thermal treatment and chemical etching for being poorly effective in highlighting microstructural features), a decision was made to observe all samples as sintered, with only a conductive carbon film as coating.

Dilatometry was performed in air using a Linseis L70 setup and bar shaped samples with about 1 cm long and 3 × 2 mm^2 cross sectional area, heated at a constant rate of 10 °C min^{-1} up to about 1600 °C.

3. Results and discussion

3.1. Structural characterization

Two 7MgPSZ samples (sintered and corresponding milled powders) were firstly studied by XRD to test the coherence of analysis using distinct software packages. The corresponding patterns are shown in Fig. 1 while the results from phase quantification are listed in Table 1.

The analysis of powder patterns is a clearly good example of reliability. All sets of data are within close values. The gross phase compositions are in the order of 30 wt% for the C phase and 70 wt% for the M phase. Looking at data for the sintered bodies the picture is totally distinct. The M phase content is obviously lower than for the milled samples but the discrimination between T and C is clearly difficult. In general we have an underestimated C phase content, quite significant in some cases. We should recall that the C phase content should be the same in the powders and sintered bodies since the conversion C → T involves cation diffusion, halted at room temperature.

There is no special surprise in these results. Almost superimposed main C and T phase peaks are hardly deconvoluted with accuracy [8,23–25]. Furthermore, MgPSZ is a multi-phasic material, situation