Determination of Yttrium and Lanthanum in Zirconium Dioxide by HPLC, X-ray Fluorescence and Neutron Activation Analyses

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Summary

Lanthania- and yttria-stabilized zirconium oxide ceramics have been examined using High Performance Liquid Chromatography (HPLC), thermal neutron activation (NA) and X-ray Fluorescence (XRF) analyses and thus determine the stabilizer content. Ceramic powders with the composition ZrO_2:x mol % La_2O_3 (x = 5, 10, 15, 20 and 33) and ZrO_2:x mol % Y_2O_3 (x = 10, 15, 20 and 25) were prepared by the citrate and the co-precipitation techniques, respectively. The lanthanum content was determined by HPLC (x = 5.09, 9.78, 14.98, 19.81 and 25.94) and NA (x = 5.15, 10.32, 17.25, 21.08 and 27.97) analyses, the yttrium content by HPLC (x = 8.5, 13.5, 17.9 and 22.1) and XRF (x = 9.9, 15.8, 20.1 and 24.9) analyses. An experimental sequence, based on continuous dilution of ceramic powder solutions, is proposed for preparing samples for HPLC measurements. A swimming pool nuclear reactor is used for NA analysis. The quantitative determinations of yttrium and lanthanum doping levels obtained using those techniques are described.

Introduction

Zirconia (zirconium dioxide) is a remarkable material that has attracted much attention due to its properties, such as chemical inertness, permeability, thermal shock resistance and ionic conductivity. Uses to which it has been applied include (among others) catalysts, gas sensors and thermal barrier coating [1]. Even though its surface chemistry is considered complex [2], it has also been proposed for use as a column packing material (support particle) for High Performance Liquid Chromatography [3, 4]. For the majority of these applications it is usual to stabilize the high temperature cubic and/or tetragonal phases. Partial or total stabilization is achieved by a chemical substitution of Ca, Mg, Y or rare earth cations (known as stabilizers) for some of the Zr ions in the ZrO_2 lattice, leading to the formation of cation vacancies as charge-compensating defects. These vacancies are known to play a major role in the stabilization mechanism [5–9]. Traditional ceramic processing methods as well as chemical methods can be used for this purpose. The former present the advantage of equal nominal and real (after sintering of the ceramic) concentrations provided that no loss of stabilizing cations occurs during the high temperature treatments normally employed. The main disadvantage of these methods is the high temperatures needed for sintering and the inhomogeneity of the specimens. In the case of chemical processing, the sintering temperatures are comparatively lower, and the final microstructures are, in general, more homogeneous. The shortcoming of the latter is that processing variables need to be rigorously controlled in order to obtain good reproducibility. Moreover, these methods are not always quantitative. For technological applications it is very important to know the exact amount of stabilizing agent, because almost all the ceramic's properties are concentration-dependent.

The techniques of HPLC, thermal neutron activation analysis and X-ray fluorescence have been used for the determination of stabilizer content in zirconia ceramics. The basic principles of these techniques are described below.

HPLC Technique

The high performance liquid chromatography method is based on dynamic ion-exchange chromatography using bonded microparticulate alkyl silica as stationary phase in combination with a low concentration of hydrophobic ions in the eluents. In this study a separation was carried out by a dynamic ion exchange on a C-18

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bonded silica reversed phase column in an isocratic elution mode with DL-latic acid buffered at pH 3.8. The elution of yttrium and lanthanum was monitored by visible spectrophotometry at 535 nm after an on line post column reaction with pyridylazoresorcinol. This technique allows for the determination of trace amounts of several elements. As the zirconia stabilizers are in the percent range, the samples had to be diluted for their determinations.

Thermal Neutron Activation Analysis

Neutron activation analysis is a method of quantitative chemical analysis based on nuclear activation of the chemical elements present in the analyzed sample. Activation analysis relies on the nuclear reaction between projectiles and target nuclei. The analyzed samples may be activated by bombardment with thermal neutrons, fast neutrons, energetic charged particles or high energy photons. Activation with thermal neutrons is the most used form of activation analysis due to larger available fluxes and relatively larger cross sections. The neutron interacts with the target nucleus, thereby converting the latter into a radioactive nucleus. As the radioactive nucleus decays back to a stable state, decay gamma-rays are emitted. The amount of emitted radiation depends on the number of atoms in the target sample. Each radioactive nuclide that is formed during irradiation decays with a specific half-life, emitting gamma-rays of characteristic energy. Measurements of the gamma radiation can be used to identify and accurately quantify the nuclides present in the sample. Subsequent to irradiation, gamma-radiation is measured in a high resolution germanium detector. Activation analysis can be used to determine either trace elements or bulk elements.

Neutron activation analysis has been widely used in characterization and quality control of high purity materials due to its high sensitivity as well as good precision and accuracy [10, 11]. For the particular case of the analysis of rare earth elements, this technique is specially appropriate, due to their high thermal neutron cross sections.

The X-ray Fluorescence Technique

The wavelength dispersion X-ray fluorescence (WDXRF) technique is effected by impinging an X-ray beam into a sample to produce fluorescence radiations that are characteristic of chemical elements in the sample. These radiations are diffracted by an analyzing crystal and directed to a detector. Calibration curves can be drawn using the relationships between the fluorescence intensities due to each element and the intensities of standard specimens.

In this work, La and Y cations have been used to stabilize zirconia ceramics by means of different processing techniques (citrate precursor and co-precipitation). The actual concentration of stabilizing cations was measured by the high performance liquid chromatography, neutron activation analysis or X-ray fluorescence analysis techniques. The main purpose of this work was to establish standard procedures to determine quantitatively the amount of yttrium and rare earth stabilizers in zirconia ceramics.

Experimental

The techniques for the preparation of stabilized ceramic zirconium oxide powders and the procedures for the analysis of the stabilizers content are described below.

The Citrate Technique [12] ZrO_2:La_2O_3

The raw materials used were zirconyl chloride (BDH), 99.6 % pure lanthanum oxide (Sigma), citric acid (99.5 %) and concentrated nitric acid both from Merck, and P.A. ethylene glycol. La_2O_3-stabilized ZrO_2 powders (5, 10, 15, 20 and 33 mol % La_2O_3) were prepared by mixing appropriate amounts of zirconyl chloride into lanthanum chloride and heating up to 90–100 °C, followed by additions of citric acid, ethylene glycol and nitric acid under continuous stirring. The resin then obtained is calcined at 1000 °C for 2 h yielding fine ZrO_2:La_2O_3 powders. The powders were pressed into pellets and sintered at 1500 °C for two hours.

The Co-precipitation Technique ZrO_2:Y_2O_3

ZrO_2:Y_2O_3 ceramic powder specimens have been prepared by the co-precipitation technique. Among the several chemical techniques for the synthesis of ceramic powders, the co-precipitation technique is the most used [13]. Four different yttria concentrations (10, 15, 20 and 25 mol %) have been added. The co-precipitation technique consisted of the following: PA sulfuric acid was added to the basic zirconium sulfate and yttrium oxide (99.9 %) in order to obtain zirconium and yttrium sulfate solutions, respectively. These two solutions were mixed in the desired proportion and precipitated with ammonia under vigorous stirring. The precipitate was repeatedly washed with water, ethanol and acetone to remove sulphate residues and water from the gel. The hydrated oxide was dried at 80 °C for eight hours. Calcination was carried out at 900 °C for one hour in air. The powders were pressed into pellets and sintered at 1500 °C for two hours.

HPLC Analysis

All solvents used were of HPLC grade and prepared with water purified in a Milli-Q unit (Millipore). Prior to its use it was filtered through a 0.2 µm membrane filter and degassed by means of an ultrasonic wave. All the reagents used were of analytical grade: 0.2 M D-L lactic acid aqueous solutions buffered at pH 3.8 with ammonium hydroxide, 0.05 mg.L^{-1} 4-(20pyridylazo) resorcinol monosodium salt (PAR) in 2 M ammonium hydroxide and 1 M acetic acid and 0.01 M sodium octanesulfo-

Table I. Values of lanthanum oxide content in ZrO_2:La_2O_3 ceramics determined by high performance liquid chromatography and thermal neutron activation analysis.

La_2O_3 content, nominal (mol %)	La_2O_3 content, HPLC (mol %)	La_2O_3 content, neutron activation (mol %)
5	5.09 ± 0.14	5.15 ± 0.26
10	9.78 ± 0.35	10.32 ± 0.19
15	14.98 ± 0.51	17.25 ± 0.37
20	19.81 ± 0.51	21.08 ± 0.41
33	25.94 ± 0.17	27.97 ± 1.34

Table II. Values of yttrium oxide content in ZrO_2:Y_2O_3 ceramics determined by high performance liquid chromatography and X-ray fluorescence analysis.

Y_2O_3 content, nominal (mol %)	Y_2O_3 content, HPLC (mol %)	Y_2O_3 content, XRF (mol %)
10	8.50 ± 0.23	9.9 ± 0.2
15	13.47 ± 0.46	15.8 ± 0.3
20	17.92 ± 0.46	20.1 ± 0.3
25	22.07 ± 0.56	24.9 ± 0.3

nate (OS). Standard metal solution were obtained from Johnson Matthey.

The HPLC system consisted of a Waters 625LC apparatus running with a linear gradient program, a Rheodyne 9125 load injection valve, a constant-flow peristaltic pump, a Waters 490 programmable multiwavelength spectrophotometric detector, a Waters RDM module post column, a Shimadzu LC10 workstation, a Waters Nova-Pak C-18 column (150 × 3.9 mm ID) and a Waters C-18 Guard-Pak (5.0 × 6.0 mm). Dilution of the samples of ZrO_2:Y_2O_3 and ZrO_2:La_2O_3 was carried out in platinum crucibles according to the sequence: 100 mg of zirconia in 1 mL of 40 % HF at 60 °C (twice) and in conc. H_2SO_4 at 100 °C up to complete evaporation, followed by dilution in 100 mL 8 % H_2SO_4. For the determination of yttrium or lanthanum, samples (20 µL) of the diluted solutions of ZrO_2 in 8 % H_2SO_4 were injected into the mobile phase, 0.2 M lactic acid and 0.01 M OS pH 3.8 with flow rate of 1 $mL.min^{-1}$. The eluted Y and La were detected after post-column reaction with PAR at 0.5 $mL.min^{-1}$ flow rate and monitored by a programmable multiwavelength detector at 535 nm at retention times of 5 min and 13.5 min for Y and La, respectively. The quantification of Y and La has been done by comparison of sample peak areas with the peak areas of some standards covering the concentration range expected for the samples.

Thermal Neutron Activation Analysis

High purity lanthanum oxide (Johnson Matthey) was calcined at 800 °C for 90 minutes. A standard solution was prepared by dissolving an accurately weighed amount of lanthanum oxide in dilute nitric acid. A convenient aliquot of the standard solution was pipetted onto a 1 cm^2 piece of Whatman No. 40 filter-paper, evaporated to dryness under an infrared lamp and packed in a polyethylene vial. Irradiation was carried out at the IEA-R1 nuclear reactor at this Institute. Aliquots of about 20 mg of the powdered sample were weighed in pre-cleaned polyethylene irradiation vessels specially developed for use in the reactor. Samples and standards were irradiated for 30 minutes at a thermal flux of 5×10^{11} $n.cm^{-2}.s^{-1}$. The measurements of the induced gamma-ray activity were carried out in an hyper pure Ge detector connected to a multichannel analyzer (ACE 8K ORTEC) and to a personal computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of ^{60}Co. The gamma-ray spectra were processed by using the program VISPECT, developed at IPEN. This program locates peak positions and calculates gamma-ray energies and net areas. The counting times were about 40 minutes. The determination of lanthanum was performed with the radioisotope ^{140}La ($t_{½}$ = 40.27 h; E_γ = 328.6 keV, 1595.4 keV) produced by the nuclear reaction $^{139}La(n,\gamma)^{140}La$. The terms $t_{½}$ and E_γ stand for the γ-decay half-life and energy, respectively.

X-ray Fluorescence Analysis

The WDXRF spectrometer consists of a Rigaku Geigerflex X-ray generator and a goniometer with 0.01°Bragg angle resolution, equipped with Rh X-ray tube operating at 50 kV and 40 mA, 150 mm collimator, NaI(Tl) scintillation detector and LiF(200) analyzer crystal. The samples and the standards are prepared as double layer pellets with boric acid as binder. Standards are Johnson Matthey spectrographic pure oxides.

Results and Discussion

Lanthanum in ZrO_2

ZrO_2:La_2O_3 ceramic powders were prepared by the citrate technique. The added values of La_2O_3 were 5, 10, 15, 20 and 33 mol %. The determination of lanthanum content was carried out by HPLC and thermal neutron activation analysis. The results are shown in Table I. The values determined by HPLC are in good agreement with the added values, even though a 200 times dilution had been carried out in the samples.

Yttrium in ZrO_2

ZrO_2:Y_2O_3 ceramic powders were prepared by the coprecipitation technique. Table II shows Y_2O_3 contents calculated after determination of yttrium by HPLC and XRF techniques.

A good agreement is shown for yttrium contents determined by XRF and HPLC analysis; the values are smaller in the latter due to losses known to occur in the dilution process used to prepare the samples.

Conclusions

Several techniques have been used for the determination of the content of yttrium and lanthanum incorporated as stabilizers in zirconia ceramics. Lanthanum content has been evaluated by High Performance Liquid Chromatography (HPLC) and Thermal Neutron Activation (NA) Analyses, and yttrium content by HPLC and X-ray Fluorescence (XRF). Experimental procedures have been determined for the preparation of samples for each analysis. The main results show that all three techniques are suitable for the quantitative determination of Y and rare earth elements in ZrO_2 ceramics. Special care must be taken for sampling HPLC specimens due to losses that might occur during the continuous dilution process.

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