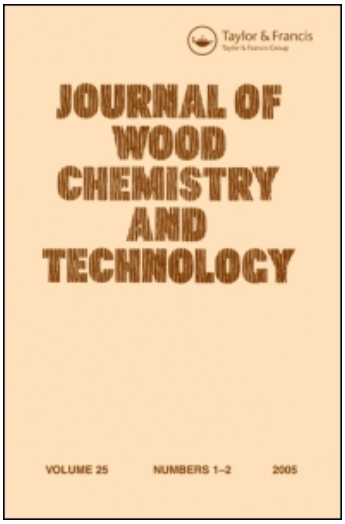

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Experimental Design in the Optimization of a Microwave Acid Digestion Procedure of Biomorphic Ceramic Based on ZrO_2

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Abstract: The present work deals with the manufacturing of biomorphous ZrO_2-ceramics from oak wood as biological template structure. Oak wood was vacuum infiltrated with zirconia-sol. Subsequent pyrolysis in inert atmosphere at 800°C and annealing in air up to 1550°C resulted in the formation of porous, microcellular ZrO_2-ceramics. After the material characterization, we optimized the sample dissolution by acid attack in an oven under microwave irradiation. Experimental designs were used as a multivariate strategy for the effects evaluation of varying several variables. The optimization was performed using full factorial design 2^4. Four variables (time, power, volume of HNO_3, and volume of HF) were considered as factors and as response the concentration of different metal ions in the optimization process.

Keywords: Biomorphic ZrO_2-ceramics, dissolution, experimental design, metal ions, synthesis

INTRODUCTION

Wood is a natural material with a novel and ordered hierarchical structure. The processing of biomorphous ceramics represents an advanced concept for manufacturing of porous ceramic materials with microcellular morphologies.

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Previous work on biotemplating was focused mainly on the preparation of biomorphous carbide ceramics, for example, SiC via a reaction of the biological material derived biocarbon with different Si-infiltrants such as Si-melt, Si/SiO-gas, Si-containing polymers as well as SiO_2-sols.[1–5] During the last years several investigations were also focused on the synthesis of biomorphic non-carbide materials. In this way, Yermolenko et al.[6] prepared Al_2O_3- and ZrO_2-fibers by oxidizing hydrated cellulose fibers impregnated with solutions of aluminum chloride and zirconium chloride. Patel and Padhi[7,8] manufactured Al_2O_3- and TiO_2-fibers by infiltration of natural sisal, jute and hemp fibers with $AlCl_3$ and $TiCl_4$, respectively. Ota et al.[9] produced biomorphous oxide ceramics by infiltration of wood materials with metal alkoxide, e.g. TTiP (titanium isopropoxide). After high-temperature treatment in air the wood structures were converted into porous TiO_2-ceramics. Shin et al.[10] synthesized hierarchical porous SiO_2-ceramics from wood by a surfactant-templated sol–gel process. Biomorphic Al_2O_3-, TiO_2-, ZrO_2- and mullite ($Al_6Si_2O_{13}$)-ceramics were prepared from rattan plants via a sol–gel process by Sieber et al.[11,12] Cao et al.[13] developed the manufacturing of biomorphous Al_2O_3-, TiO_2-, and ZrO_2-ceramics from pine wood as biological template structure. The same research group proposed the synthesis of biomorphic, highly porous ZrO_2 ceramics from natural performs.[14]

Sieber presented a very interesting work whose aim was to discuss the technological approaches for the different biomimetic conversion methods as well as characteristic properties and applications of the resulting biomorphous ceramics and ceramic composite materials.[15] Studart et al.[16] reviewed the main processing routes that can be used for the fabrication of macroporous ceramics with tailored microstructure and chemical composition. The recent progress in the synthesis of wood-derived ceramics from natural templates is summarized by Luo et al.[17]

Ultrafine zirconia particles have wide applications in the production of advanced ceramics, dense films, ultrafiltration membranes, and so on. The potential use of nanosized zirconia in the fabrication of dense ceramics is based on its unique set of properties, such as high refractivity, corrosion resistance, mechanical strength, fracture toughness, and ion conduction.[18]

The main objective of this work is the optimization by experimental design of a process of acid digestion using microwave oven of a biomorphic ceramics previously synthesized and characterized by us to determine the content of some metal ions whose they are present in the native wood due to they can have effect over the physical properties of the ceramic, so one biomorphic materials derived from oak wood has been synthesized. XPS has been used for to verify the content of ZrO_2 after the preparation of the biomaterial samples. AAS has been used after the previous microwave dissolution of the samples; dissolutions of the samples have been optimised by using acid attack under microwave irradiation.

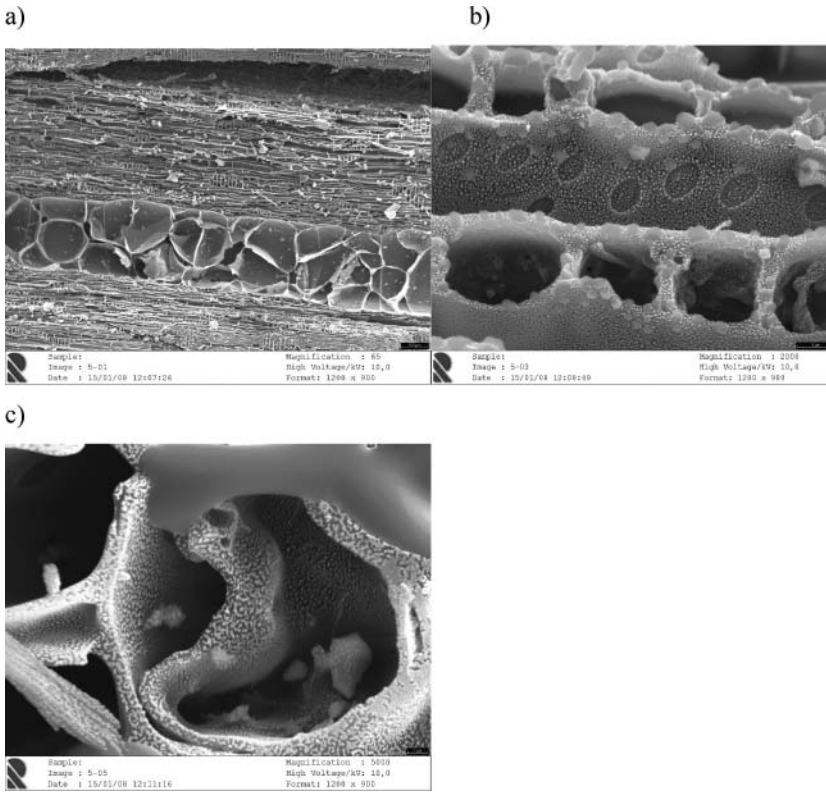

Figure 1. Micrographs of biomorphic ceramic obtained with SEM at different magnification. a) ×65, scale 1:100 μm; b) ×2000, scale 1: 5 μm; c) ×5000, scale 1:1 μm.

EXPERIMENTAL

Instrumentation

A Lenton Tube furnace, model LTF 16/180, was employed for the synthesis of biomorphic ceramics.

X-ray photoelectron spectroscopy (XPS) analysis was performed with a Physical Electronics 5700 instrument with a MgKαX-ray excitation source (hν = 1253.6 eV); binding energies (BE) were determined with respect to the position of the Ca2p peak at 346.5 eV. The residual pressure in the analysis chamber was maintained below 10^{-9} Torr during data acquisition.

Scanning electronic microscopy (SEM) JEOL, Model 840 was used to obtain the micrographs shown in Figure 1.

A Panasonic (National) microwave oven, model NN-8507, and a Parr Microwave Acid Digestion Bomb, model 4782, were used for sample digestion.

The bombs were cleaned before use with 10% nitric acid for 1 day followed by repeated rinsing with water.

A Varian Model SpectrAA 50 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer was used for the analysis with the appropriate hollow cathode lamp.

Powder patterns were collected on a X'Pert Pro MPD automated diffractometer equipped with a Ge(111) primary monochromator (strictly monochromatic CuKα_1 radiation) and an X'Celerator detector. The overall measurement time was ∼30 min per pattern to have very good statistic over the 2 range of 10–70° with 0.017° step size. The patterns were identified using the PDF (Powder Data File).

Reagents

Analytical reagent grade chemicals were used throughout. Zirconium oxychloride octahydrate (Merck). Standard 1000 μg mL^{-1} Fe(III), Ca(II) and Mg(II) solutions (Fluka) were used. Standards of working strength were made by appropriate dilution as required, immediately prior to use. Water was deionized with a Milli-Q system. Concentrated acid HCl, HF, H_2SO_4, and HNO_3 (Merck) were used for digestion of the samples.

Synthesis

Rectangular specimens of native oak were dried (70°C/15 h) and subjected to vacuum infiltration for 15 min with ZrO_2-sols.[18] The specimens were dried at 110°C for 1 h in air to form the gel in the wood cells after infiltration. A schematic diagram of the device used for the vacuum infiltration is shown in Figure 2.

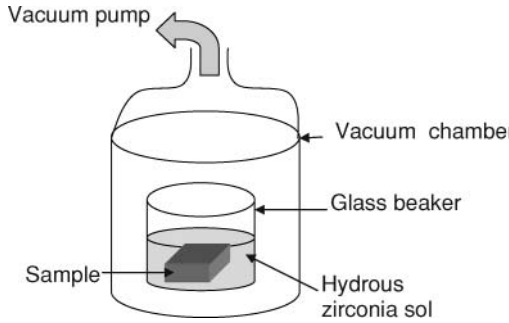

Figure 2. Schematic drawing of the experimental set-up for the vacuum infiltration process.

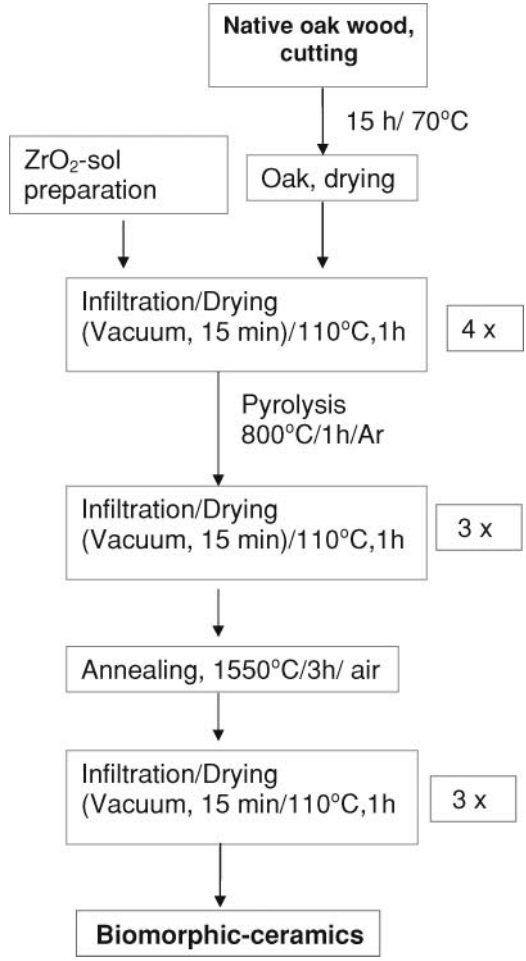

Figure 3. Flow chart for the manufacturing of biomorphic ZrO_2 ceramics.

The infiltration and drying process was repeated for four times. Multiple infiltrations were used to increase the content of the ZrO_2 precursor in the specimen. After the infiltration steps, the oak samples were pyrolyzed at 800°C for 1 h in Ar atmosphere in order to decompose cellulose, hemicellulose, and lignin into carbon. After repeated infiltration steps, the specimens were annealed up to 1550°C during 3 h (temperature ramp 10°C/min up to 1550°C). The infiltration/drying process was repeated up to three times to increase the ZrO_2 content in the biomorphic samples. The infiltration/annealing processing are described by the schematic diagram in Figure 3.[14]

Table 1. Mixtures of acids tested for the microwave-assisted dissolution of ceramic material

Order	Mixture of acids
1st	4 mL HCl + 1 mL HF
2nd	4 mL HNO_3+ 1 mL HF
3rd	4 mL H_2SO_4+ 1 mL HF
4th	1 mL HNO_3+ 3 mL HCl (aqua regia)
5th	4 mL HCl + 4 mL H_2SO_4
6th	4 mL HNO_3+ 4 mL H_2SO_4
7th	3 mL HCl + 1mL HNO_3+ 1 mL HF
8th	4 mL HCl + 1 mL H_2SO_4+ 1 mL HF
9th	3 mL HCl + 4 mL H_2SO_4+ 1 mL HNO_3
10th	4 mL H_2SO_4+ 4 mL HNO_3+ 1 mL HF

Microwave-Assisted Pressure Digestion with Acids

In a preliminary step, mixtures of acids were employing following the order given in Table 1. The volume of these mixtures is taken randomly. For this test, 10 mg of sample accurately weight and the corresponding acid mixture was added to the digestion vessels and was treated for 2 min to 700 W. The dissolution obtained was completely transferred into a 25 mL calibrated flask and diluted to volume with water. Then, these dissolutions were measured by Flame atomic absorption spectrometry (FAAS) and taking as response variable the concentrations of several ions to select the better mixture of acids. From these data we concluded the best acid mixtures were (HNO_3+ HF).

Later, a two-level 2^4 full factorial design with 16 runs (in duplicates) was developed in order to determine the influence of the factors and their interactions on the system. Four factors were studied: digestion time, microwave radiation applied power, and volumes of acids selected (HNO_3 and HF).

The sequence of the experiments carry out is shown in Table 2. The experimental data were processed making use of the STATGRAPHICS 5.1 plus program.[19] The significance of the effects was done by analysis of variance (ANOVA) and using p-value significance levels. This value represents the probability of the effect of a factor being due solely to random error. Thus, if the p-value is less than 5%, the effect of corresponding factor is significant. The effects and significance of the variables in the microwave-assisted digestion system were evaluated using Pareto's charts.

RESULTS AND DISCUSSION

The microstructure of the fabricated material is shown in Figure 1 at different magnification: in axial (a) and tangential direction (b,c).

Table 2. Design matrix and the results for Fe, Ca, and Mg concentrations

Experiment	HNO_3 (mL)	HF (mL)	Power (W)	Time (min)	Fe μg mL^{-1}	Ca μg mL^{-1}	Mg μg mL^{-1}
1	6	3	560	2	1.05	1.19	2.53
2	6	6	560	2	1.36	2.13	2.87
3	3	3	560	3	1.36	4.31	1.64
4	3	6	560	3	1.05	4.94	4.42
5	6	3	560	3	2.14	9.63	2.88
6	6	6	700	2	1.36	4.94	3.26
7	3	3	700	3	2.61	3.69	2.98
8	6	3	700	3	1.36	3.38	2.02
9	3	6	700	2	1.20	6.50	2.10
10	3	6	560	2	1.67	0.88	2.48
11	6	6	700	3	1.20	3.38	2.96
12	6	6	560	3	1.67	4.63	4.64
13	6	3	700	2	0.42	5.88	3.26
14	3	3	560	2	1.52	0.88	2.59
15	3	6	700	3	1.52	1.19	2.86
16	3	3	700	2	2.77	1.81	2.26

XPS Analysis

XPS has been used for the study of the surface composition of the sample. For this study the biomorphic materials were powdered and homogenized in an agate mortar. Measurements were performed on samples mounted in a cup (1 mm $\times$ 3.5 mm i.d.) and pressed manually.

XPS spectrum obtained is shown in Figure 4. Consequently, the performance of the synthesis of biomorphic ceramics can be evaluated approximately from these data.

The atomic concentration calculation is expressed as a percentage in a tabular form based on the area under the peak, multiplied by the sensitivity factor for each element, and provides a ratio of a single element to the sum of the others elements present[20] (Table 3). The error of the method is approximately of 10%.

XRD Analysis

The identification is based on PDF data base. The content of amorphous phase in the sample is high as can be seen from Figure 5, due to the background curvature between 20–30° 2 theta and 40–50° 2 theta. From this figure we can conclude the sample is especially monoclinic ZrO_2 (PDF number

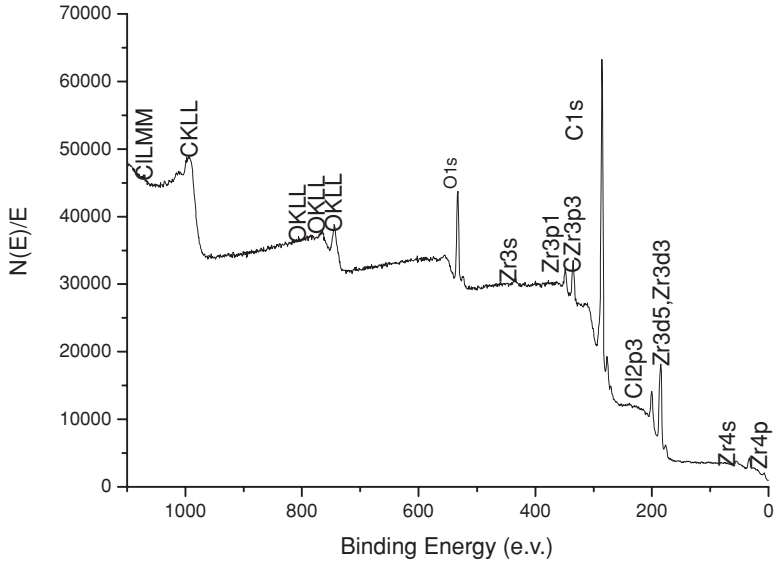

Figure 4. XPS survey spectrum for biomorphic ceramic from oak wood.

01-086-1450), although the sample shows in less proportion tetragonal phase of the same oxide (PDF number 01-080-0784).

Sample Dissolution

Factorial design approach is an useful tool to establish and improve analytical procedures. Although it seems more complex than the univariate procedure from the operative point of view, it is advantageous because it makes use of fewer experiments and provides important information on interactions among

Table 3. Analysis of biomorphic sample by XPS

		Concentration (%)	
Element	Area (cts-eV/s)	Atomic	Mass
C1s	146125	82.44	61.72
O1s	47588	10.73	10.7
Zr3d	56081	3.69	20.98
Cl2p	15198	2.89	6.39
N1s	730	0.25	0.22

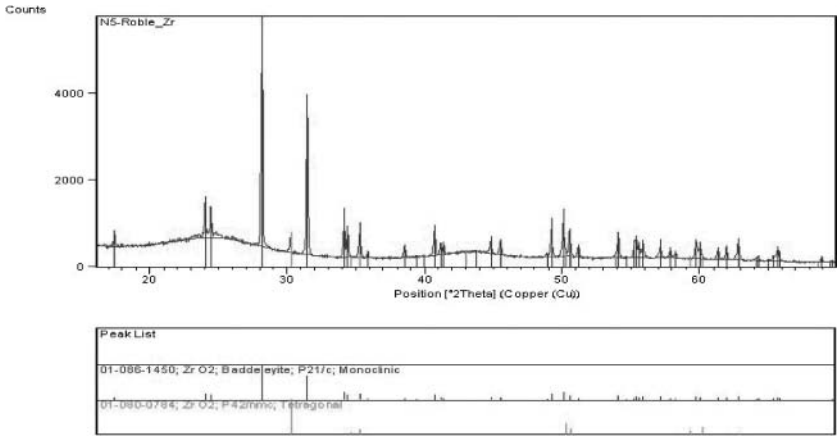

Figure 5. XRD spectrum for biomorphic ceramic from oak wood.

the studied variables.[21,22] A two-level full factorial 2^4 with 16 runs was carried out in order to determine the main factors of the microwave-assisted biomorphous ZrO_2-ceramic digestion. The results of the ANOVA carried out on the data given in Table 3 are shown in Table 4.

In this experiment, a negative value for the effect means an inversely proportional effect on metallic ion concentrations and a positive value means a directly proportional effect on metallic ion concentrations, as can be seen in Figure 6a, b, c. The results considering Ca concentration as response (Figure 5a), demonstrated that the most significant effect was the interaction of microwave applied power and time. The interpretation of the factorial design

Table 4. *p*-value for data analysis given in Table 3 for metal ions concentrations

Source	Ca	Mg	Fe
A: Volume HNO_3	0.1734	0.3102	0.1759
B: Volume HF	0.7650	0.1041	0.3198
C: Power	0.7650	0.4298	0.7682
D: Time	0.1740	0.3158	0.4691
AB	0.3089	0.8217	0.1448
AC	0.7650	0.8649	0.0793
AD	0.6999	0.5206	0.2189
BC	0.5281	0.1935	0.4691
BD	0.1550	0.1111	0.3934
CD	0.0133	0.2991	0.8787

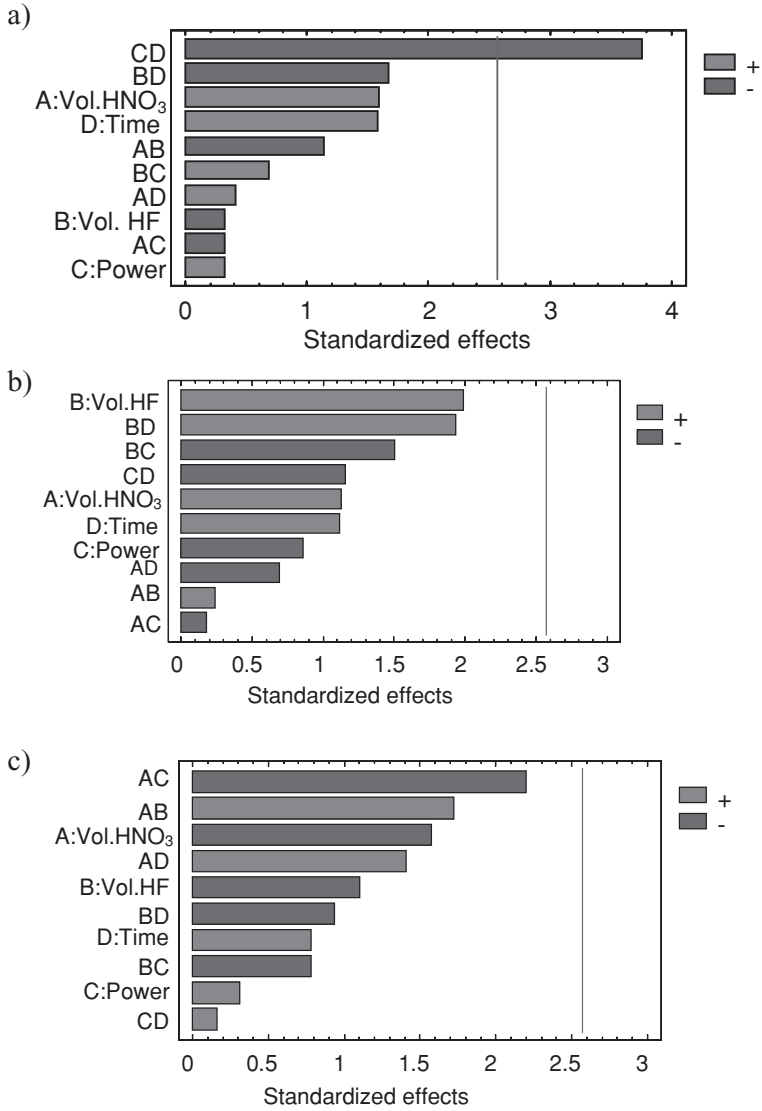

Figure 6. Pareto's charts for: a) Ca; b) Mg; c) Fe.

by Pareto's chart in Figure 5b and Figure 5c using Mg concentration and Fe concentration, respectively, as response shows that the studied variables do not have significant effects. The optimum values for the determination of each metal ion are shown in Table 5.

Table 5. Optimum values of the factors for metal ions determination

Factor	Ca	Mg	Fe
Volume HNO_3	6	6	3
Volume HF	3	6	3
Power	560	560	700
Time	3	3	3

CONCLUSIONS

In this work, we have synthesized a new ceramic material by infiltration with $ZrOCl_2$ from oak wood. The application of factorial design allowed the optimization of parameters that influence the performance of microwave-assisted acid digestion procedures. Employing the Pareto's charts, it was possible to evaluate the influence of each variable and the combination of variables in the metallic ion concentrations. The determination of metal ions in this ceramic can be achieved by acids dissolution under microwave irradiation, followed by FAAS analysis. Dissolution under microwave irradiation shortens appreciably the time of the acid attack.

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