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Multivariate optimization of the synthesis and of the microwave dissolution of biomorphic silicon carbide ceramics

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ABSTRACT

Biomorphic silicon carbide ceramics are a new class of materials that are used for various industrial applications owing to its attractive properties. The efficiency of the synthesis and the partly extreme properties of the biomorphic ceramic depend decisively on the synthesis parameters and on the impurities of the final ceramic. In the present article the synthesis as well as the decomposition of these materials is optimized using a multivariate methodology for the design of experiments. Three variables (initial amount of Si, infiltration temperature and reaction time) were considered as factors in the synthesis optimization and six variables (digestion time, ramp time, microwave power, volumes of concentrated HF, HNO_3 and H_2SO_4) in the microwave dissolution optimization. Interactions, between analytical factors and their optimised levels were investigated using full factorial, Plackett–Burman and central composite designs. The synthesis parameters that found higher percentage of SiC (quantified by FTIR) and the digestion procedure that found higher concentrations of metals (Co, Cr and Ni, determined by FI-ETAAS) were considered the optimum.

1. Introduction

Biomorphic ceramics are materials made by a transformation of biological preforms into a ceramic material. Different applications are promising for such materials, especially for SiC ceramics, because of their good performance, including high-temperature stability, high mechanical strength, high thermal conductivity and chemical inertness towards acids and bases [1–3]. These materials are used in structural applications (machine and cutting tools, wear components, aerospace components, and biomedical implants) and in electronic applications (insulators, capacitors, transducers, electronic sensors, and electrooptical elements).

The synthesis of these new materials is based on the infiltration of the pyrolized wood templates with silicon; there are several ways of synthesis: infiltration with molten silicon [4–7], chemical Si contained vapor infiltration (CVI) [8,9], infiltration–pyrolysis of metallic-alkoxide [10], polymeric precursors [11], sol–gel infiltration/carbothermal reduction [12–14], etc. Between them, the chemical vapour infiltration produces SiC ceramics with very good properties; however, the cost is high compared with the infiltration with molten silicon. In this last technique, biomorphic SiC ceramics are made by a two step process: a controlled pyrolyzation of the wood followed by a rapid controlled reactive infiltration of the wood preform with molten silicon. The diversity of wood species provides a wide choice of materials, in which the density and the anisotropy are the critical factors of the final microstructure and hence of the mechanical properties of the material. This manufacturing process presents several advantages over others: lower cost reduces the temperatures of process and the use of additives or high purity powders and faster, because the time and the synthesis rates are reduced.

The properties of these materials are greatly influenced by the stoichiometric molar ratio of the macroconstituents, and also by the presence of impurities [15], even at very low concentrations. Furthermore, small amounts of dopants [16], sintering aids [17] and other additives are added to these ceramics in order to improve their processing and ultimate properties. Because of this, the determination of elements in advance ceramics is crucial to manufacturing control, property improvement, failure prevention and quality assurance. However, the chemical composition of the biomorphic materials has been scarcely investigated. For the chemical analysis of these refractory and chemically resistant materials by atomic spectrometry, complete dissolution of the samples with extreme chemical treatments must be performed. The microwave-assisted pressure digestion is a promising alternative for sample preparation owing to the advantages over acid decomposition and alkaline fusion procedures: strict control of the heating power, ability to use small volumes of reagents, lower reagent blank, etc. Matusiewicz [18] evaluated a commercial laboratory microwave acid digestion system for the acid dissolution of ceramic powders (Al_2O_3, AlN, BN and Si_3N_4) prior to the determination of their trace element content by microwave induced plasma atomic emission spectrometry. Mann et al. [19] compared various wet chemical digestion procedures, such as pressure

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digestion, microwave-assisted pressure digestion and decomposition via alkaline fusion for the dissolution of new advanced ceramic materials, with subsequent determination of the main components Si and B by sequential inductively coupled plasma atomic emission spectrometry (ICP-AES). Larrea et al. [20] compared the detection limits obtained for some elements by ICP-AES in the dissolution of electronic advanced ceramics by acid microwave-assisted heating and alkaline fusion. Also they compared the analytical results obtained in the determination of impurities by ICP-AES in a lead titanate-based ceramic. Electrothermal atomic absorption spectrometry (ETAAS) is one of the most popular techniques for ultra-trace analysis owing to its high sensitivity and low detection limit. Applications of ETAAS are found in analyzing industrial materials such as silicon dioxide powder [21]. However, matrix interferences and/or a very low analyte concentration usually cause difficulties in the direct measurement of the analyte. The coupling of flow injection (FI) on-line column preconcentration/separation techniques to ETAAS has proved to be effective for this purpose [22]. Experience in our laboratory and the consulted bibliography [20,23] has shown that for the dissolution of materials with high levels of Si (SiC), the mixture of $HNO_3 + H_2SO_4 + HF$ under microwave-assisted pressure digestions can be used.

In the present work, we have optimized the experimental conditions for the synthesis and for the dissolution of this type of materials. The procedures were optimized by resorting a full factorial design for the synthesis [24]; and a Plackett–Burman screening design [25] and central composite design (CCD) [26,27] for the microwave dissolution. For the evaluation of the quality of the process of synthesis of these biomorphic ceramics, SiC was quantified in the synthesized ceramics by Fourier transform infrared spectroscopy (FTIR) [28]. For the optimization of the microwave-assisted pressure digestion, a FI on-line column preconcentration system coupled to ETAAS was developed in this work for the determination of the low concentrations of cobalt, nickel and chromium present in the biomorphic ceramics. Three variables (initial amount of Si, infiltration temperature and infiltration time) were considered as factors in the synthesis optimization and six variables (digestion time, ramp time, microwave power, volumes of HF, HNO_3 and H_2SO_4) in the microwave dissolution optimization. The variables that did not have a significance effect on the responses were screened out, and the remaining factors affecting the procedures were optimized using a CCD. This type of design allows the experimental domain to be mapped and optimal values for parameters to be deduced, while reducing the number of experiments compared to a sequential design. Understanding the main factors and their interactions permitted the development of a mathematical model to predict instrumental response.

2. Experimental

2.1. Reagents and samples

High-purity reagents were employed in all experiments. The KBr pellets were prepared with potassium bromide and barium acetate from Merck (Darmstadt, Germany). Pure silicon and silicon carbide (99.999%, w/w) were purchased from Aldrich Chemie (Steinheim, Germany). All these reagents were dried at 48 °C for 24 h and after conserved into a desiccator. Analytical reagent grade HNO_3 (65%), H_2SO_4 (97%), and HF (48%) (Merck, Darmstadt, Germany) were used as reagent for dissolution procedures. Doubly deionised water with a resistivity 18.2 $M\Omega\,cm^{-1}$, produced by a Milli-Q water system (Millipore, Bedford, MA, USA) was used throughout. Standards solutions 1000 $\mu g\,ml^{-1}$ Co, Ni and Cr (Fluka, Buchs, Switzerland) were used. Standards of working strength were made by appropriate dilution as required, immediately prior use. Ascorbic acid (Merck) 1000 $\mu g\,ml^{-1}$ was used for cobalt determination. A pH 8.5 buffer was prepared by mixing boric acid (Merck) 0.2 M with NaOH (Merck) until pH 8.5 was reached.

Different kinds of biomorphic ceramics derived from natural woods (oak, beech, Swedish pine and eucalyptus) have been used. The synthesis and characterisation of 1,5-bis(di-2-pyridyl)methylene thiocarbonohydrazide (DPTH-gel) chelating resin were described in a previous paper [22]. Argon with a purity of 99.99%, was used as the internal gas during analysis and synthesis of the biomorphic ceramics.

2.2. Instrumentation

The infrared spectroscopic measurements were carried out using a Shimadzu Model 8300 Fourier transform infrared spectrometer. The spectra were recorded in the range 2000–500 cm^{-1} with a resolution of 2 cm^{-1}. Potassium bromide pellets were used to obtain the IR spectra of the samples. The pellets with 13 mm diameter and 0.4 mm thickness were pressed at 8 tonnes for 10 min in an evacuated pellet die from 90.0 mg mixture sample, barium acetate and potassium bromide. For the mass measurements an AND GR-202 balance was used with a precision of ± 0.01 mg. Multivariate calibration data was carried out using Statgraphics Plus 6.0 professional software [29].

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

The ETAAS measurements were carried out using a Perkin-Elmer (Norwalk, CT, USA) Zeeman/4100ZL, atomic absorption spectrometer with a longitudinal Zeeman effect background correction system, equipped with an AS-70 furnace autosampler. The standard transversely heated graphite atomizers (THGA) with integrated pyrolytic graphite platforms were used. Cobalt, nickel and chromium cathode lamps (Perkin-Elmer) were used at a wavelength of 240.7, 232.0 and 357.9 nm, respectively, with a spectral bandpass of 0.7 nm for Cr and 0.2 nm for Co and Ni.

The samples were digested using an Anton Paar (Graz, Austria) Multiwave 3000 microwave oven equipped with a XF-8 rotor and XF-100 digestion vessels. After digestion the solutions were evaporated into the EVAP rotor.

The microcolumn containing the DPTH-gel was a glass tube (3 cm × 3 mm i.d.) packed to a height of 0.5 cm; at both ends of the microcolumn, polyethylene frits (Omnifit, Cambridge, UK) were fixed to prevent material losses. On the end of this column was placed a piece of sample capillary of the sampler arm (in imitation of the sample tip of the sampler arm). Thus the sample tip of the sampler arm was replaced with this microcolumn. This connection is extremely simple, and permits full use of the original software. A peristaltic pump (Gilson Minipuls 3, Williers, France), fitted with a vinyl pump tube (1.65 mm i.d.) was used for loading of the sample. A Rheodyne (Cotati, CA, USA) Type 50 six-port rotary valve was used as a switching valve. Transport lines were made using 0.5 mm i.d. Teflon tubing. A schematic diagram of the circuit and peripherals was shown in a previous paper [30].

2.3. Synthesis of the biomorphic ceramics

Rectangular specimens of wood (beech) were cut with dimensions of (15 mm × 10 mm × 10 mm) in axial orientation. The carbon performs were prepared by pyrolyzing the dried (70 °C, 15 h) wood in argon-atmosphere. A slow heating rate of 1 °C/min was applied up to 500 °C where the organic biopolymers have been completely decomposed to carbon followed by an accelerated rate of 5 °C/min up to 1000 °C. This temperature was held for 4 h, resulting in a porous biocarbon template (charcoal). Each charcoal was placed in a boron nitride-coated alumina crucible with an appropriate amount of silicon powder. Compared to the carbon, the silicon was in molar excess up to a factor of 2.5 to aid in the conversion of the charcoal to SiC. Carbon and silicon were heated in vacuum to a temperature higher than 1410 °C at which point the silicon became molten and was wicked into the porous carbon template. The system was held at that temperature for different times to allow the reaction to progress. The