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Quantitative determination of ZrC in new ceramic materials by Fourier transform infrared spectroscopy

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Abstract

Zirconium carbide-based biomorphic ceramics have been manufactured by vacuum infiltration of zirconium-oxychloride ($ZrOCl_2{\cdot}8H_2O$) sol into natural wood. After vacuum-assisted infiltration, the specimens were dried in air and pyrolysed at 800 °C in Ar-atmosphere. The infiltration and drying process were repeated up to four times. Finally, the specimens were hold at 1550 °C in a vacuum furnace to form ZrC. The results of the process of synthesis have been studied using scanning electron microscopy (SEM). For evaluating the yield of the synthesis, a new method by Fourier transform infrared spectrometry (FTIR) has been developed for the direct determination of ZrC by absorbance measurements in KBr pellets. The procedure was based on the use of the ratio between the absorbance of the characteristic band of zirconium carbide and those of an oxalate internal standard added to samples. A multivariate calibration strategy based on inverse least squares and the standard addition approach was employed for quantification. The results obtained for all ZrC-ceramics studied were satisfactorily compared with those obtained by X-ray diffractometry (XRD). The proposed method was also applied to the analysis of synthetic samples prepared by mixing pyrolyzed wood with ZrC, the results indicated good recovery in all instances.

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1. Introduction

ZrC as one of ultra-high temperature ceramics, combines the characteristics properties of metals and ceramics due to ionic, covalent, and metallic bonding simultaneously in its NaCl-type lattice structure. ZrC exhibits various outstanding physical and chemical properties, such as high hardness, high melting point, high corrosion and wear resistance, solid-state phase stability as well as chemical stability. Hence, ZrC has been considered a good potential material for ultra-high temperature applications [1].

Generally, ZrC powders can be economically produced through reacting power mixtures of carbon (C) and zirconium metal (Zr), zirconium hydride (ZrH_2) or zirconium oxide (ZrO_2) at comparatively high temperature above 1800 °C for several hours. In these methods, high temperatures are needed for the formation of ZrC, because the starting materials are mixed on a relatively coarse-scale (micrometer range). Recent studies have shown that ZrC can be synthesized at lower temperatures using precursors [2].

In recent years, a new type of porous ceramic materials with specific functional properties and structures by mimicking the hierarchical cellular structure of wood has attained particular interest. These ceramic materials, called biomorphic ceramics, show at low density excellent mechanical properties such as high-strength, stiffness, toughness, good oxidation and corrosion resistance, high-thermal conductivity, and good thermal shock resistance.

While in biological growth and mineralization processes only very slow material synthesis rates occur, biotemplating techniques, in which biological materials are used directly as template structures for high-temperature conversion into technical ceramic materials, overcome this time rate problem [3]. The inherent open porosity in the natural plant structures is accessible for gaseous or liquid infiltration and subsequent high-temperature ceramic phase formation. Previous work on

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biotemplating was mainly focused on the manufacturing of biomorphous SiC-based ceramics 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 [4–6]. During the last decade several investigations were also focused on the synthesis of biomorphic transition metal carbides (e.g. ZrC, TiC) [7]. Compared to SiC, the mechanical properties, such as modulus of elasticity, compressive strength and fracture toughness of ZrC and TiC-based ceramics are inferior, but they are characterized by a higher melting point, and specially, a nearly metallic electrical conductivity [8]. Thus, ZrC-based ceramics is a promising candidate for a wide range of high temperature applications.

The sol–gel method is one of the newer methods for synthesizing ceramic materials, owing to low cost, no troublesome procedure, and allowing lower temperatures of synthesis. The synthesis of biomorphic TiC and ZrC-carbides from wood templates by infiltration of Ti- and Zr-alkoxides has been reported by Rambo et al. [9] Also, these authors compared the synthesis, the final composition and the morphology of porous, biomorphic Me-carbide (Me = Si, Ti and Zr) manufactured via infiltration of low viscosity oxidic sols into biologically derived biocarbon templates from pine wood [10]. For the evaluation of the quality of the process of synthesis of these biomorphic ceramics the quantitative determination of Me-carbide is very interesting. As there are no adequate certified reference materials available for the calibration of analytical methods for the characterization of this new class of compounds no direct methods could be used. Fourier transform infrared spectroscopy (FTIR) is potentially a good tool for the structural studies of these types of materials, however up to now it has not been widely used; only Qian and Jin [11] have employed this technique to investigate the carbothermal conversion of the charcoal silica composites into SiC in the final step of the synthesis. Our investigations have shown that Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) are the most useful devices to obtain fast information about the content of silicon carbide in the sample, [12] although XPS is a semiquantitative technique.

FTIR is a rapid analytical technique that provides information about the qualitative composition of samples. However, quantitative analysis by FTIR requires the use of cells of known thickness and, in general, a previous dilution of the sample with a suitable solvent, limitations which often preclude the general application of this technique to quantitative determinations. In recent years, a series of simple models for carrying out quantitative determinations from infrared data, which do not require the use of a known absorption pathlength, have been described [13]. These models are based on the use of the ratio of the absorbances at two well-defined wavenumbers, however, the use of the ratio of the characteristic bands of two compounds in a mixture does not permit the determination of the concentration of each component, and only the proportion of the two compounds considered was obtained. This problem can be solved if the concentration of one of the compounds is known; thus it is possible when this compound is an adequate internal standard [14].

In a previous work we reported [15] strategies which could be used for routine determination of SiC in biomorphic ceramics based on the use of FTIR absorbance measurements in KBr pellets. Due to the good results obtained, the main objective of this work was to exploit the potential of the FTIR technique for evaluating the yield of the synthesis of biomorphic ceramics. Thus, in the present paper a method has been developed for routine determination of ZrC in biomorphic ceramics based on the use of FTIR. Four different woods of varying density and pore size were chosen as precursors, softwood (lime), three hardwoods (oak, cherry and beech). The results obtained for all ceramics studied were satisfactorily compared with those obtained by X-ray diffractometry (XRD). The proposed method was also applied to the analysis of synthetic samples prepared by mixing pyrolyzed wood with pure ZrC, the results indicated good recovery in all instances.

2. Experimental

2.1. Reagents

Analytical reagent grade chemicals were used throughout. Potassium bromide, and disodium oxalate were purchased from Merck (Darmstadt, Germany) and zirconium carbide (99.5%, w/w) from Aldrich Chemie (Steinheim, Germany). Zirconia sol was obtained from zirconium oxychloride ($ZrOCl_2{\cdot}8H_2O$, 99.9%, Alfa Aesar). All reagents were dried at 48 °C for 24 h and after conserved into a desiccator.

2.2. Sample preparation

Different kinds of biomorphic ceramics derived from natural woods (oak, beech, lime and cherry-wood) were prepared for the sol–gel infiltration process. The preparation of the samples was based on a procedure described by Rambo et al. [10]. $ZrOCl_2{\cdot}8H_2O$ (zirconium oxychloride) was used as precursor for infiltration and subsequent conversion into zirconia. It provides a viable route for producing of fine ZrO_2 particles. The precursor sol, $ZrOCl_2{\cdot}8H_2O$ (48 g) was dissolved in 40 ml of 0.05 M HCl and mixed with 60 ml of 0.05 M HCl under vigorous agitation. The mixture was refluxed and stirred for 24 h. After cooling to room temperature, the resulting sol was immediately used.

Rectangular specimens (3 cm × 1 cm × 0.6 cm) of the carbon preform were cut perpendicular to the native wood axis. The samples were dried at 70 °C for 15 h, and subsequently vacuum infiltrated (15 min) with the zirconia sol. The infiltrated samples were dried in air at 130 °C for 2 h to form the gel in the wood cells after infiltration. This procedure was repeated up to four times to achieve a higher content of the ZrO_2 precursor in the wood. After, the samples were pyrolyzed at 800 °C for 1 h in Ar-atmosphere. At this temperature the biopolymers (cellulose, hemicellulose and lignin) of wood were decomposed, leaving a porous carbon char. During pyrolysis a low heating rate ($1.5\ ^{\circ}C\ min^{-1}$) was adopted to avoid damage in the wood cell walls by gas release. The infiltration and drying process was repeated up to four times to increase the ZrO_2 content in the biomorphic samples. Finally the specimens were hold at 1550 °C for 1 h in Ar-atmosphere to allow complete reaction of zirconia with the carbon structure to form ZrC, this carbothermal reduction is the most common method to produce MeC-ceramics:

$$MeO_2 + 3C \rightarrow MeC + 2CO$$

The processing scheme is summarized in Fig. 1.

2.3. Instrumentation

The content of zirconium carbide in the samples was monitored by FTIR and X-ray diffractometry (XRD, D 500, Siemens, Kar-lsruhe, Germany).

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 4 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 of sample, disodium oxalate and potassium bromide. For the mass measurements an AND GR-202 balance was used with a precision of ±0.01 mg. Multivariate calibration data treatment was carried out using Statgraphics Plus 6.0 professional software [16].

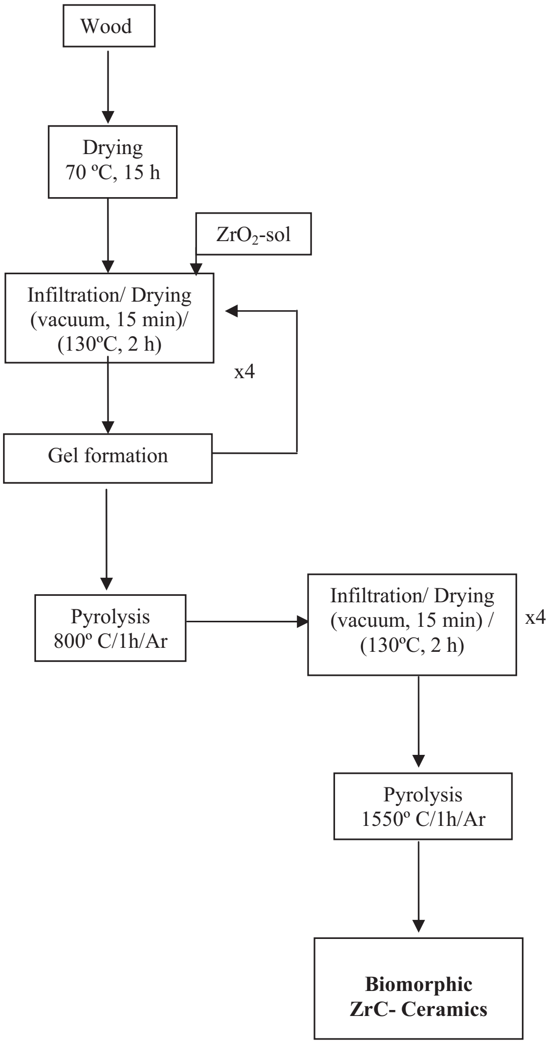


Fig. 1. Processing scheme of manufacturing ZrC ceramics from wood.

A Lenton Tube furnace, model LTF 16/180, was employed for the synthesis of biomorphic ceramics. The cellular microstructures of the biomorphic ceramics were observed by scanning electron microscopy (SEM, JEOL, JFM 840) operated at 20 kV.

2.4. Preparation of standard addition calibration set for ZrC determination

KBr pellets were prepared by mixing different accurately weighted amounts from 0.00 to 2.50 mg (±0.01 mg) of ZrC, 1.00 mg (±0.01 mg) biomorphic ceramic (previously grounded and homogenized), 1.00 mg (±0.01) internal standard (sodium oxalate), and KBr to complete a total amount of 200.0 mg (±0.1). The mixture was homogenized for 5 min in an agate mortar, and then 90.0 mg (±0.1 mg) of this were weighted for the pellets preparation. Else six blanks were prepared in the same form but mixing 1.00 mg (±0.01 mg) internal standard and 199.0 mg (±0.1 mg) KBr. For the background spectrum, a pellet was prepared with 90.0 mg (±0.1 mg) KBr.

The spectra were recorded from 2000 to 500 cm^{-1}, using a nominal resolution of 4 cm^{-1} and accumulating 50 scans for spectrum. Peak area measurement corresponding to ZrC band (1383 cm^{-1}) was divided by data corresponding to the 1634, 1332 and 776 cm^{-1} oxalate bands, using baselines given in Table 1, and ZrC determined by multivariate calibration strategy of inverse least squares, using the standard addition approach as a function of added mg of the ZrC, from absorbance quotient data of six blanks prepared as described above. The baselines were chosen with the pellet spiked with a 1 mg ZrC.

2.5. Standard addition analysis using an internal standard and multivariate calibration strategy by inverse least squares

In this paper, the standard addition method using an internal standard was used as described by us in a previous work [15]. In multivariate calibration strategy by inverse least squares, several instrumental responses ($r_1, r_2, r_3, \ldots r_n$) can be used and the analyte concentration can be calculated as:

$$[ZrC]_{sample} = b_0 + b_1 r_1 + b_2 r_2 + b_3 r_3 + \ldots + b_n r_n$$

where b_0, b_1, b_2, b_3 and b_n are the regression coefficients.

Table 1
Baselines established for integrating areas.

ν (cm^{-1})	χ_{min} (cm^{-1})	χ_{max} (cm^{-1})
1634	1580	1730
1383	1360	1408
1332	1275	1350
776	752	795

In our case the instrumental response are the quotients between the peak area corresponding to ZrC (1383 cm^{-1}) divided by the peak areas corresponding to the 1634, 1332 and 776 cm^{-1} disodium oxalate bands:

$$r_1 = \frac{A_{1383}}{A_{1634}}; \quad r_2 = \frac{A_{1383}}{A_{1332}}; \quad r_3 = \frac{A_{1383}}{A_{776}}$$

So, an equation with four unknowns (b_0, b_1, b_2, b_3) is obtained. If l added samples for measurement, there will be a system of l equations with four unknowns. Obviously, must be made at least four additions. When the regression coefficients are calculated, the determination of ZrC in the sample is done in the same form rather than in standard additions with univariate calibration, by means of the measurement of a blank.

3. Results and discussion

3.1. Characterization of the biomorphic ceramics

According to Rambo et al. [10], the weight of the specimens after repeated sol-infiltration and drying cycles shown that the number of infiltration steps and thus the weight increase is limited by the clogging of the pores on the surface of the specimens by the gel, which inhibited further infiltration after approximately 4 cycles. However, parts of the bulk volume of the specimens were still incompletely infiltrated. On the other hand, a large weight loss of the zirconia sol as well as of the biological wood material during pyrolysis and sintering processing was observed. The major weight loss is related to the carbonization of the native wood (the weight loss of native wood is about 70–80 wt.% [17]), as well as to the water and HCl evaporation from the zirconia sol.

3.2. SEM analysis

The cellular microstructure of the biomorphic ceramics is shown in Fig. 2. During the reactive infiltration processing, zirconia infiltrates through the pores and channels of the pyrolized wood structure and reacts with the carbon. Softwoods have one type of pore in the plane perpendicular to the growth direction (axial plane) while hardwoods tend to have two types of pores in this plane, hardwoods can be classified as uniformly distributed pore (UDP) and not uniformly distributed pore (NUDP) [18], in the micrographs shown in this paper, the different types of pores and the differences in the uniformity of pore distribution are evident. As can be seen in Fig. 2, the large pores (black area in the micrographs) have not been completely filled with ZrC. So, complete conversion of the biocarbon char template into ZrC was not achieved for any of the wood used. The hardwoods UDP (beech and cherry) with smaller pores uniformly distributed show higher convertion to ZrC. Thus, depending on the type of wood, a significant difference in morphology and in ZrC yield is found in the experimental conditions used.

3.3. XRD study

XRD has been used for the study of the composition of the samples. As an example, the XRD pattern of biomorphic ceramic from beech is shown in Fig. 3. Distinct peaks of the cubic ZrC can be observed at $2\theta = 33.1°$, 38.4°, 55.4°, 66.1° and 69.4°; in addition to these lines the peak at $2\theta = 25.2°$ can be attributed to carbon and the peak at $2\theta = 41.5°$ can be attributed to B_2Zr from boron nitride-coated alumina crucible. The degree of conversion of the biocarbon char template into ZrC depends on the type of wood according to the SEM analysis. Other weak peaks were attributed to impurities present in the samples.

3.4. FTIR determination of ZrC

3.4.1. Selection of the appropriate bands for the FTIR measurement of ZrC

Fig. 4(A) shows the FTIR spectra of KBr pellets of pure ZrC and sodium oxalate. The band at 1383 cm^{-1} was attributed to Zr–C stretching, this band was assigned in comparison with the spectrum of pure ZrC. The bands at 1634, 1332 and 776 cm^{-1} were assigned to stretching vibration of C–O bond and to deformation of –COO, respectively, of sodium oxalate [19]. As can be seen from Fig. 4(A) the oxalate bands not overlapping with the band of the ZrC, so these bands are appropriate to be employed for ZrC determination in order to avoid the problems related to establish quantitative data in conditions for which it is difficult to fix the bandpass.

Fig. 4(B) shows the FTIR spectrum of a KBr disk with 0.5% of biomorphic ceramic plus 0.5% of sodium oxalate. As can be seen, in the spectrum appear the three characteristics band of sodium oxalate and the band at 1383 cm^{-1} ascribed to the Zr–C fundamental stretching vibration.

3.4.2. Selection of the instrumental parameters and conditions of measurement

Absorbance measurements in the solid phase are usually affected by levels of noise larger than those found in homogenous solution due to the presence of the solid support, which causes a strong attenuation of the light intensity reaching the detector. Thus, a careful study of the instrumental parameters and conditions of measurement was carried out in order to obtain as good as possible signal-to-noise ratio, which would then ensure satisfactorily reproducible data.

The ZrC band at 1383 cm^{-1} and the sodium oxalate bands at 1634, 1332 and 776 cm^{-1} were used in this study. Heights were measured at these wavenumbers and areas were calculated by drawing the baselines shown in Table 1. The ratios of the band heights (or areas) were used, obtaining the best results with the areas ratios.

A systematic study of the effect of the nominal resolution and the number of accumulated scans was performed under the aforementioned conditions. The number of accumulated scans per spectrum was changed from 20 to 250, and the nominal resolution varied from 0.05 to 32 cm^{-1}. An increase in the number of cumulated scans has no influence on the ratio of the bands (heights or areas) but it reduces the background

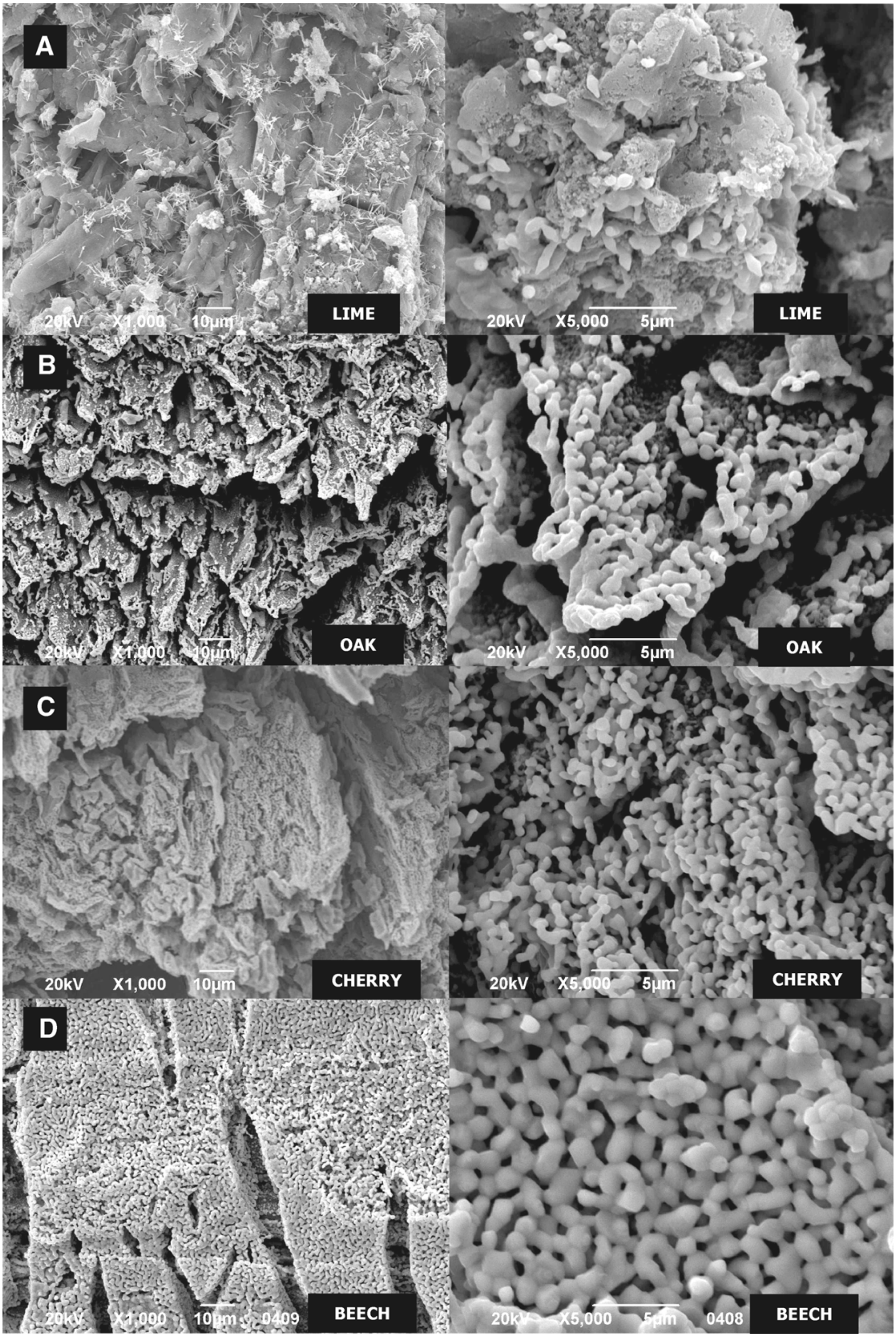


Fig. 2. SEM micrographs of biomorphic ceramics. (A) Lime, (B) oak, (C) cherry, (D) beech.

drastically. So, 50 scans were established as suitable FTIR measurements in order to ensure a compromise between measurements frequency and precision values. On the other hand, the more intense signals were found for a 4 cm^{-1} nominal resolution, this value also corresponding to the best repeatability.

Due to the darkness of the KBr disks of the biomorphic ceramics, the amount of sample for preparing the disk and the

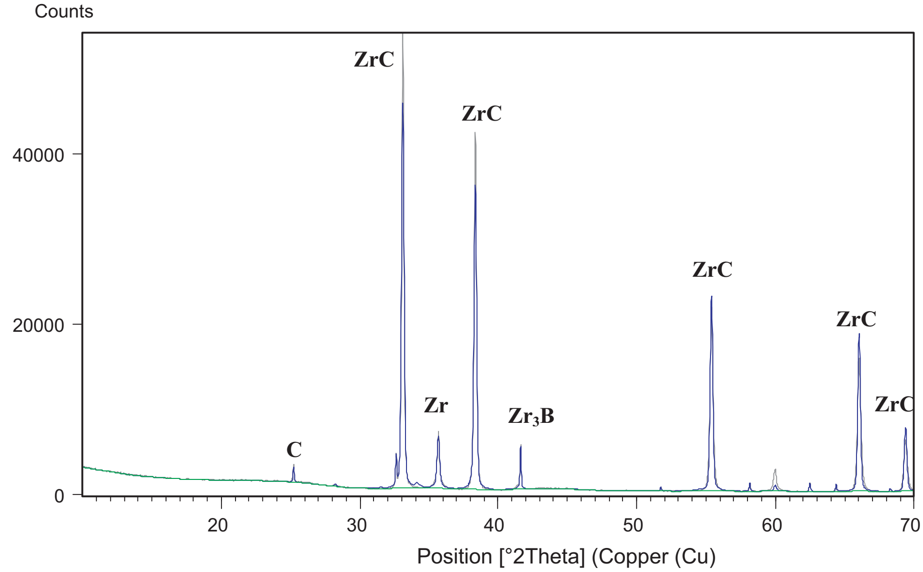


Fig. 3. XRD spectrum of biomorphic ceramic from beech.

total weight of the pellet had to be optimized; the amount of biomorphic ceramics was varied from 0.5 to 2.5 mg maintaining the total weight of the mix in 200 mg and taking 90 mg of the homogeneous mix for preparing the pellet; the more intense signal at the interest bands was that with 1 mg of sample (0.5% in biomorphic ceramic), with this concentration in biomorphic ceramic the total weight of the pellet was varied from 60 to 150 mg. A decrease in the weight of the disk produces more transparent disks, but more fragile, so 90 mg were established for suitable FTIR measurements in order to ensure resistant KBr disks.

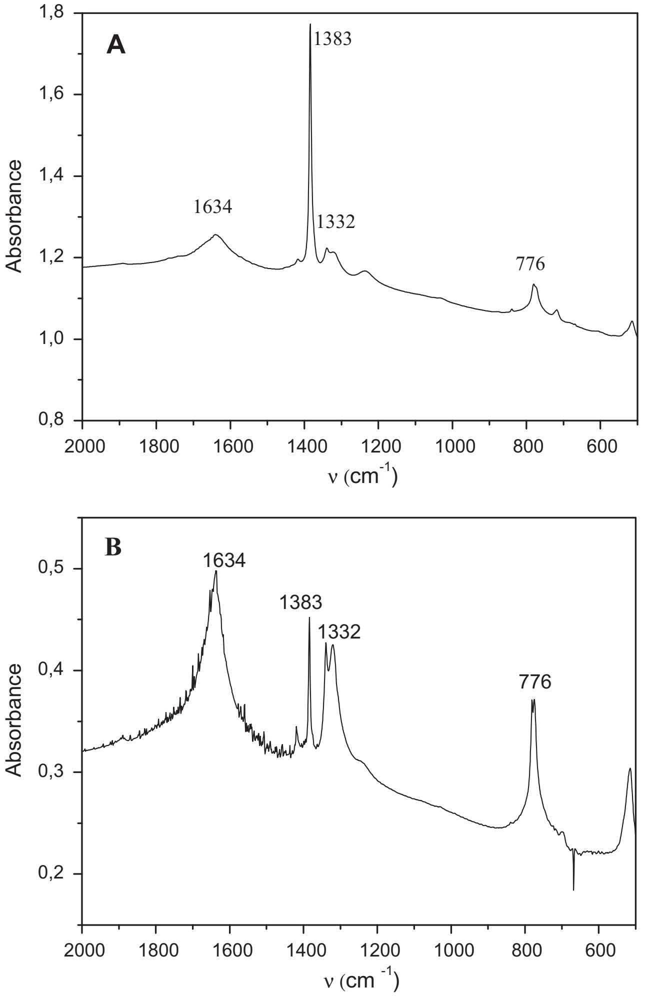
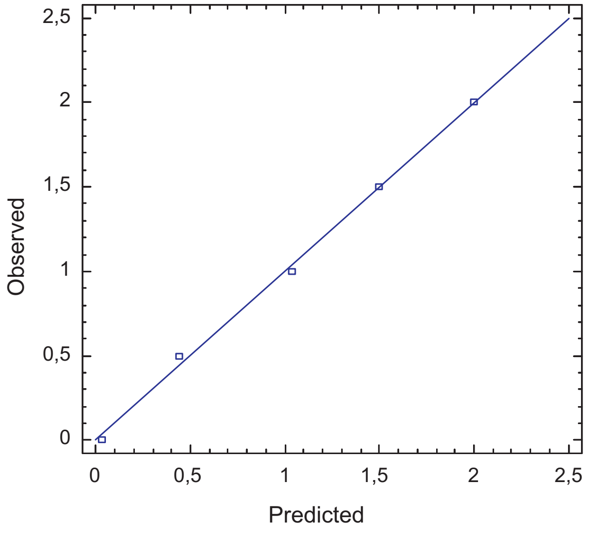


Fig. 4. FTIR spectra of KBr disks of pure ZrC and sodium oxalate (A), biomorphic ceramic plus 0.5% of sodium oxalate (B).



[ZrC] = 0.886546 + 10.4239*Ar1383:Ar1332 + 2.04625*Ar1383:Ar1634 + 0.101064*Ar1383:Ar776

R- squared = 99.791 percent
R-squared (adjusted for d.f.) = 99.1639 percent
Standard error of Est. = 0.0722867

Fig. 5. The observed vs. predicted graphs and the equation of the fitted model for the biomorphic ceramic from beech for ZrC determination.

Table 2
Results of the determination of ZrC in biomorphic ceramic by XRD and FTIR.

Biomorphic ceramics from	XRD (% ZrC)	FTIR (% ZrC)
Oak	55.8 ± 0.3	59.4 ± 1.5
Cherry	62.6 ± 0.3	64.2 ± 8.6
Lime	51.4 ± 0.3	59.3 ± 1.7
Beech	74.7 ± 0.3	78.5 ± 6.9

Table 3
Results of the determination of ZrC for synthetic samples.

Content of the synthetic samples (% ZrC)	FTIR analysis (% ZrC)
0.0	−0.0060 ± 0.0002
25.0	26.2 ± 1.2
50.0	47.8 ± 1.1
75.0	75.3 ± 1.0
100.0	99.8 ± 0.4

3.4.3. *Quantitative analysis of FTIR data*

The KBr disks of the biomorphic ceramics are darker than those of pure ZrC, and so a method of external calibration could not be possible, being necessary use standard additions. Simple linear regression (SLR) and multiple linear regression (MLR) were proved with each of the three ratios of areas chosen between the analyte and the internal standard, obtaining the best results with the MLR method. Calibration lines were prepared by addition of 0.00–2.50 mg of ZrC. The peak area values of the interest bands were calculated using the baselines given in Table 1. As an example, the observed versus predicted graph and the equation of the fitted model for the biomorphic ceramic from beech for ZrC determination are given in Fig. 5.

The results obtained for all biomorphic ceramics studied (Table 2) were satisfactorily compared with those obtained by XRD analysis, although the percentages obtained with FTIR were higher than those obtained with XRD. This fact can be explained because the results obtained with XRD are wt.% in crystalline phase and likely there is some of zirconium carbide in the amorphous phase. As can be seen from Table 2, depending on the type of wood, a significant difference in ZrC yield is found, this is in good agreement with the SEM observations. The hardwoods with uniformly distributed pore (UDP) (cherry and beech) provide higher percentages of ZrC. To test the applicability of the method, synthetic samples were prepared by mixing pyrolyzed wood with pure ZrC and were analysed by the proposed method. The results shown in Table 3 indicated good recovery in all instances.

4. Conclusions

The results presented in this paper for ZrC in biomorphic ceramics show that FTIR using the ratio of absorbance peak areas between the analyte and a reference compound, provides accurate results for the determination of this compound in the samples without the need to use cells with a known optical pathlength. This method can be used satisfactorily in the evaluation of the quality of the processes of synthesis of these new materials because the preparation of these samples as KBr pellets is the simplest and the most rapid form to realize these analyses; so as to allow its applicability in the industrial field, where short times are always a priority.

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References

[1] X. Tao, W. Qiu, H. Li, T. Zhao, Synthesis of nanosized zirconium carbide from preceramic polymers by the facile one-pot reaction, Polym. Adv. Technol. 21 (2010) 300–304.

[2] Y.S. Nam, X.M. Cui, L. Jeong, J.Y. Lee, W.H. Park, Fabrication and characterization of zirconium carbide (ZrC) nanofibers with thermal storage property, Thin Solid Films 517 (2009) 6531–6538.

[3] P. Greil, Biomorphous ceramics from lignocellulosics, J. Eur. Ceram. Soc. 21 (2001) 105–118.

[4] E. Vogli, J. Mukerfi, C. Hoffmann, R. Kladny, H. Sieber, P. Greil, Conversion of oak to cellular silicon carbide ceramic by gas-phase reaction with silicon monoxide, J. Am. Ceram. Soc. 84 (2001) 1236–1240.

[5] C. Zollfrank, R. Kladny, H. Sieber, P. Greil, Manufacturing of anisotropic ceramics from preceramic polymer infiltrated wood, Ceram. Trans. 129 (2002) 43–50.

[6] U. Vogt, A. Herzog, T. Graule, R. Klingner, T. Zimmermann, Porous ceramics derived from wood, Key Eng. Mater. 206 (2002) 1941–1944.

[7] H. Preiss, L.M. Berger, K. Szulzewsky, Thermal treatment of binary carbonaceous/zirconia gels and formation of Zr(C, O, N) solid solutions, Carbon 34 (1996) 109–119.

[8] E.K. Storms, The Refractory Carbides, Academic Press, London, UK, 1997.

[9] C.R. Rambo, J. Cao, H. Sieber, Biomorphic (Si, Ti,Zr) – carbide synthesized through sol–gel process, Ceram. Trans. 166 (2005) 49–55.

[10] C.R. Rambo, J. Cao, O. Rusina, H. Sieber, Manufacturing of biomorphic (Si, Ti, Zr)-carbide ceramics by sol–gel processing, Carbon 43 (2005) 1174–1183.

[11] J.M. Qian, Z.H. Jin, Preparation and characterization of porous, biomorphic SiC ceramic with hybrid pore structure, J. Eur. Ceram. Soc. 26 (2006) 1311–1316.

[12] J.M. Cano Pavón, E. Vereda Alonso, M.T. Siles Cordero, A. García de Torres, Use of spectroscopic techniques for the chemical analysis of biomorphic silicon carbide ceramics, Anal. Chim. Acta 528 (2005) 129–134.

[13] S. Garrigues, M. de la Guardia Cirugeda, Mathematical models for the Fourier transform infrared spectroscopic determination of *ortho*-, *meta*- and *para*-xylene in xylol, Analyst 116 (1991) 1159–1166.

[14] S. Garrigues, M. de la Guardia Cirugeda, Fourier transform infrared analysis of paint solvents, Anal. Chim. Acta 242 (1991) 123–129.

[15] E. Vereda Alonso, A. García de Torres, M.T. Siles Cordero, J.M. Cano Pavón, Quantitative determinations of SiC and SiO_2 in new ceramic materials by Fourier transform infrared spectroscopy, Talanta 75 (2008) 424–431.

[16] Statgraphics Plus Versión 6.0 Reference Manual, Manugistics, Rockwille, MD, 1992.

[17] P. Greil, T. Lifka, A. Kaindl, Biomorphic cellular silicon carbide ceramics from wood. I. Processing and microstructure, J. Eur. Ceram. Soc. 18 (1998) 1961–1973.

[18] V.S. Kaul, K.T. Faber, R. Sepúlveda, A.R. de Arellano López, J. Martínez-Fernández, Precursor selection and its role in the mechanical properties of porous SiC derived from wood, Mater. Sci. Eng. A 428 (2006) 225–232.

[19] K. Ito, H.J. Bernstein, The vibrational spectra of the formate, acetate and oxalate ions, Can. J. Chem. 34 (1956) 170–178.