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Synthesis, morphological and structural properties of bio-SiC ceramics

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Biomorphic SiC ceramics prepared by forced infiltration with liquid silicon of carbon matrixes derived from hardwood precursors were investigated. Phase composition of obtained ceramics was found to depend on the mass ratio of the initial silicon and carbon components, synthesis temperature and duration. Raman spectroscopy investigation shows that 3C polytype is formed at synthesis temperature ~1550°C, and both 3C and 6H SiC are formed at temperatures up to 1800°C. Further temperature rise up to 2100°C increases the fraction of 6H polytype. The study of Raman scattering also revealed the presence of residual silicon inside SiC pores. Analysis of the parameters of phonon peaks allowed us to assume that the residual silicon is under significant compressive strain. The use of surface enhancement effect of Raman scattering allowed to detect residual carbon clusters in bio-SiC.

Исследована биоморфная SiC керамика, изготовленная методом принудительного просачивания жидким кремнием углеродных матриц, полученных из натуральной древесины твердых пород. Выявлено, что фазовый состав керамики зависит от массового соотношения исходных компонент кремния и углерода, температуры и продолжительности синтеза. Исследования с помощью спектроскопии комбинационного рассеяния показали, что политип 3C образуется при температуре ~1550°C, и оба политипа 3C и 6H SiC образуются при увеличении температуры до 1800°C. Дальнейшее возрастание температуры до 2100°C увеличивает долю 6H политипа. Также выявлено присутствие остаточного кремния внутри пор SiC. Анализ параметров фононных линий позволил установить, что остаточный кремний находится под значительным напряжением сжатия. Использование эффекта поверхностного усиления интенсивности КРС позволило выявить кластеры остаточного углерода в био-SiC.

1. Introduction

During the last decade, great efforts have been devoted to the synthesis of functional materials derivated from different biological objects. Such materials are pseudomorphic to the initial biological objects in micro-, meso-, and macro scale. The interest in manufacturing of these materials is caused by relative simplicity of technology and possibility to produce materials with hierarchically connected porous structures, which is impossible when using other techniques. The biomorphic SiC (bio-SiC) derived from different kinds of wood [1] is among the aforementioned materials. The interest in bio-SiC production and its prospective applications originates from combination of unique properties of common crystalline SiC and inherent characteristics of bio-SiC.

The procedure of bio-SiC obtaining starts from pyrolysis of natural wood in an inert atmosphere (argon or nitrogen). This process results in decomposition of wood organics into volatile components and remaining porous carbon skeleton. To transform the carbon matrices into SiC, different techniques are used, such as infiltration with liquid silicon [2, 3], reactive infiltration with SiO vapor, chemical vapor infiltration [4, 5] etc. It is of fundamental importance for these processes that wood has open porous structure, thus making it suitable of such infiltration. As a result, porous SiC material is formed which preserves the microstructure of the initial wood precursor. This technique of SiC synthesis is characterized with relatively low cost and simplicity of obtaining samples from wood of desired shape.

In [2, 3], bio-SiC was obtained by spontaneous carbon skeleton infiltration with liquid Si at 1500–1600°C. In our work, the bio-SiC was synthesized using the forced infiltration method.

It is to note that implants in the human body are among the most promising applications of bio-ceramics [6–8]. The biocompatibility of the ceramic composites based on β-SiC/Si, β-SiC/C, α-SiC/Si, and α-SiC/C may differ significantly. Moreover, the mechanical and elastic properties of these materials may be also very different. Therefore, to develop a controllable technology of biomorphic SiC composites, in this work we investigated the influence of the technological factors on the phase and composition of the ceramics obtained. In particular, studied were the influence of the synthesis temperature in the 1550–2100°C range and mass ratio between carbon matrix and silicon on phase and component composition of bio-SiC ceramics derived from different wood precursors.

2. Experimental conditions

Synthesis of bio-SiC ceramics consisted of several stages. The first stage is the preparation of carbon skeleton from various wood species. The wood pyrolysis in the flow of inert gas (argon or nitrogen) at 900°C was used for that aim. In order to obtain relatively uniform pore size distribution in the bulk sample, different types of natural hardwoods with diffusive porous patterns were used, such as Europian Walnut (*Juglans regia*), European Hornbeam (*Carpinus betulus*) and pear tree (*Pyrus domestica*).

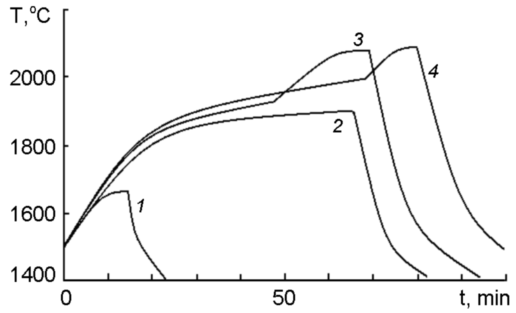

Fig. 1. Typical temperature-vs-time modes of infiltration/synthesis processes.

The second stage is forced infiltration of the obtained carbon matrix with liquid silicon resulting in SiC synthesis. The carbon matrices were placed in individual graphite crucibles and heated at the synthesis temperature in helium atmosphere. Due to the wetting forces and additional forced absorption [9, 10], liquid silicon has penetrated inside carbon matrix being involved in the synthesis reaction: $C_{sol} + Si_{liq} \rightarrow SiC$.

The maximum synthesis temperature T_{max} for different samples has been varied from 1550 to 2100°C, the process duration, from 15 to 70 min (Fig. 1, modes *1–4*), and carbon matrix/silicon mass ratio $\psi = Si/C$ has been varied within 2.0 to 3.5 range. The vacuum chamber volume in the experimental setup provided the infiltration/synthesis process to be carried out involving 20–30 samples simultaneously. It has been shown in [10] that the component composition of the SiC/Si/C composite depends on Si/C mass ratio (ψ) of initial components inside the crucible and other technological conditions. In order to obtain stoichiometric SiC composition of the final product, initial components have to react completely, and their mass balance has to be $\psi = 2.33$. At lower silicon amount ($\psi < 2.33$), SiC/C composite with relatively empty pores is formed, while $\psi > 2.33$ results in SiC/Si composite with silicon filled pores.

The structure and composition of the obtained materials were examined using optical microscopy, scanning electron microscopy (SEM), and Raman spectroscopy (RS). The RS was the principal study method. Raman spectra have been recorded using a T-64000 spectrometer for micro- and a DFS-24 one for macro-scale studies. The 488 nm wavelength of the Ar^{+} ion laser was used for excitation in both cases. Raman spectra

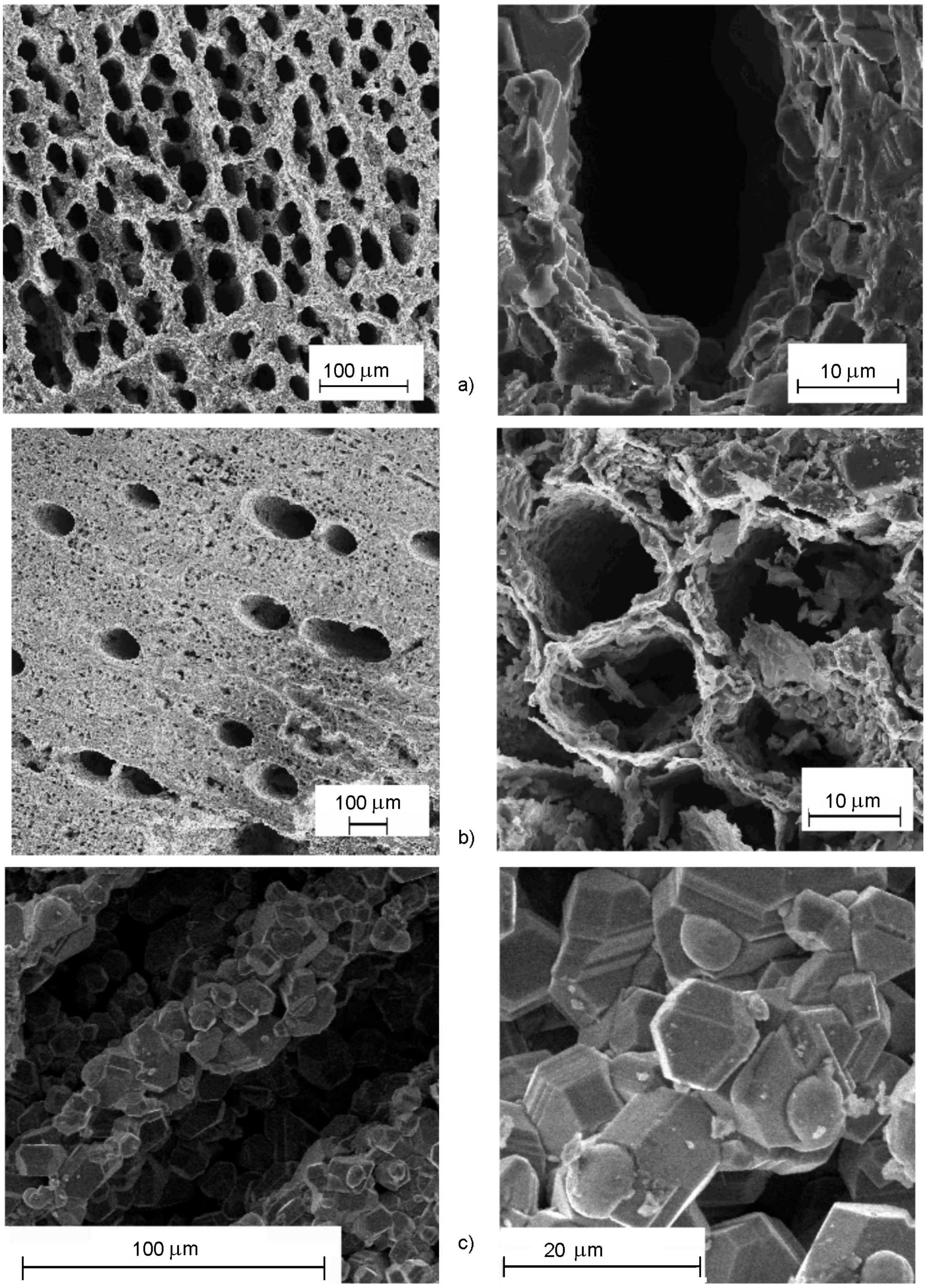

Fig. 2. SEM images of axial section surface structure of SiC ceramics derived from: (a) pear-tree wood for mass ratio $\psi < 2.33$, (b) nut-tree wood for $\psi = 2.33$, and (c) longitudinal profile of SiC ceramics derived from hornbeam wood for $\psi = 2.33$.

analysis provides the determination of the obtained SiC polytypes as well as the mechanical stress, the structural perfection degree and presence of amorphous (crystalline) phase in samples. To investigate the microstructure and micro impurities in prepared samples, the micro-Raman spectroscopy has been used. The intensity of Raman bands is found to be dependent on the laser spot position, obviously because of the SiC microcrystal or Si cluster dominating in the probed small sample volume.

3. Results and discussion

Fig. 2a and 2b show SEM microscopy images of the bio-SiC ceramics derived from different wood precursors in the plane perpendicular to the tree growth direction and Fig. 2c, in the plane parallel thereto. At higher resolution provided by SEM, synthesized microcrystals forming the SiC matrix can be clearly seen (Fig. 2, right).

It is well known that utilization of different synthesis methods always causes discrepancy in the reproducibility of natural precursor initial morphology. So, for the carbon matrix infiltration with silicon vapor, a critical pore diameter exists (about 1 μm), below which the vapor penetration occurs very slowly. On the other hand, there is a maximum pore diameter of ~120±80 μm, which still provides the spontaneous infiltration [2]. The use of forced infiltration method allows to weaken these limitations and widen noticeably the "useful" pore size range, and even to get pores completely filled with Si for certain pore sizes.

Fig. 3 shows Raman spectra in the TO band region for bio-SiC samples prepared at different temperatures. The hornbeam sample (mode *1*, T_{max} = 1570°C) shows a band at 798 cm^{-1} (spectrum 1), which corresponds to cubic 3C modification, while at increase of the synthesis temperatures up to T_{max} = 2100°C (mode 3), the spectra include three bands peaked at 767.8, 788.6 and 798 cm^{-1}, indicating formation of the 6H polytype.

The behavior of the pear-tree samples is somewhat different. As it is seen in Fig. 3 (spectra *3* and *4*), both synthesis temperatures provide SiC of the 3C modification. However, it should be mentioned that at higher synthesis temperature, T_s = 2100°C (mode *4*), the spectrum reveals a weak contribution of 6H polytype in the form of a shoulder peaked at 790 cm^{-1}. The fact of the above specific polytypes formation at the temperatures mentioned is confirmed by the scattering on folded acoustic phonons of 6H polytype in the low-frequency spectral region (spectra are not presented).

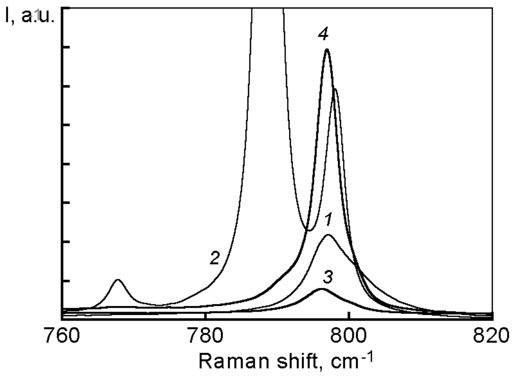

Fig. 3. Raman spectra of bio-SiC derived from hornbeam wood at 1570°C (*1*) and 2100°C (*2*) and from pear-tree wood at 1900°C (*3*) and 2100°C (*4*).

It should be noted that Raman spectra of bio-SiC ceramics prepared from nut-tree are similar to those for bio-SiC ceramics prepared from the pear-tree. For simplicity sake, these spectra are not shown in Fig. 3.

The 3C–SiC polytype is considered to be stable at temperatures below 1400°C, and can be transformed into 6H polytype at higher synthesis temperatures. The 6H polytype is the stable SiC form at temperatures above 2000°C [11]. It is well known that SiC polytype transformation may occur

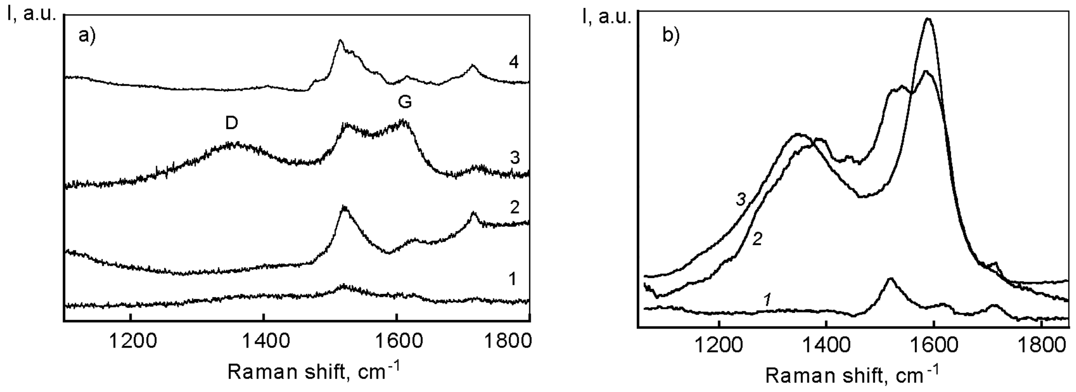

Fig. 4. Raman spectra at C–C vibrations region of: (a) bio-SiC derived from pear-tree wood at 1900°C (*1*) and 2100°C (*2*) and from hornbeam wood at 1570°C (*3*) and 2100°C (*4*); (b) bio-SiC derived from nut-tree wood, (*1*) bio-SiC, (*2*) bio-SiC covered with nanostructured silver film, (*3*) carbon C shown for comparison.

at different thermodynamic conditions: under heating in various environments, mechanical stress (bending, compression) [12], etc. Such polytype transformation can also be stimulated by introduction of impurities. Indeed, it is shown [13] that Al doping of 3C–SiC leads to 3C → 6H polytype transition. Structural and point defects in β-SiC crystals may also induce polytype transformation [14]. Fig. 1 shows that infiltration/synthesis processes were carried out at gradual temperature increase. Therefore, one can assume that the first synthesis stage where the temperature is relatively low gives rise to formation of 3C–SiC microcrystals, which may further transform into 6H–SiC after long-time heating at higher temperatures.

For the C–C vibrations investigation, the SiC/C composites obtained at $\psi < 2.33$ mass ratio of initial components are the most informative ones. Spectroscopic analysis of these structures in C–C vibration region (1100–1800 cm^{-1}) has shown that spectra of samples formed at temperatures as high as 1900–2100°C (Fig. 4a, spectra *1*, *2*, *4*) contain Raman bands corresponding to overtone and two-phonon combinations of states from Γ-, X-, and L-points of SiC Brillouin zone [15]. For the hornbeam bio-SiC obtained at $T_{max} = 1570°\mathrm{C}$ (mode *1*), along with the aforementioned bands, strong Raman bands at 1355 and 1607 cm^{-1} are present, corresponding to carbon vibrations (so-called *D*- and *G*-band, respectively). The *D* peak arises from the A_{1g} vibration mode of the sp^2 bonds in the aromatic rings of disordered graphite. The *G* peak is due to the E_{2g} vibration mode of all the sp^2 bonds in graphite [16]. That is, the bio-SiC obtained at this specific synthesis regime contains carbon clusters not transformed into SiC.

However, of great interest is to investigate the probable presence of non-reacted carbon at other ψ values. The direct Raman spectra measurements of bio-SiC samples obtained at different Si/C mass ratio do not show characteristic lines of C–C vibrations in this region, only second order lines of Si–C vibrations are present (Fig. 4b, spectrum *1*). That is why it is of great interest to make more accurate analysis of such samples to discover possible presence of residual carbon at low concentrations. To that aim, the surface enhanced Raman spectroscopy is the best solution.

In order to get surface enhancement effect, silver nanoparticle film was deposited on the bio-SiC surface by immersion plating method. It is well known that immersion of silicon containing material into solution where Ag^+ ions are present results in spontaneous silver ions reduction and silver nanoparticles formation on the surface [17]. Silver nanoparticle formation is caused by Ag^+ reduction through Si–H bonds on the surface. Thus,the samples were previously placed into HF solution for a few seconds to clean their surface and form S–H bonds thereon. Then silver film was deposited by immersion plating in 10^{-2} M $\mathrm{AgNO_3}$ solution during 5 min. As a result, silver nanostructured film is formed on the bio-SiC surface.

The Raman spectra measurements of metallized bio-SiC samples reveal intense peaks corresponding to carbon atom vibrations, namely *D* and *G* lines at 1357 and 1587 cm^{-1} (Fig. 4b, spectrum *2*). This indicates that at the corresponding bio-SiC synthesis mode (1900°C), carbon clusters not transformed into SiC are present in the resulting structure. As far as surface enhancement of Raman signal from the substance takes place only at its contact with metallic nanostructures, this shows that silver film formed by immersion plating produces surface enhancement effect for residual carbon clusters and SiC located under the film.

The Raman spectra of the SiC/Si composites reveal unusual spectral features in the region of Si–Si vibrations (Fig. 5). Instead of band at about 520 cm^{-1} typical for silicon macro- and/or nanocrystals, we observed several bands in the region of 520–540 cm^{-1} with their shape dependent on the synthesis conditions. The intensity of those Raman bands is especially high for composites with the mass ratio $\psi > 2.33$. The appearance of those bands in the mentioned spectral region may be caused by several factors. First, a substantial biaxial compression of silicon inclusions inside the pores may result in the TO-LO split of F_{2g} optical mode of the Brillouin zone center with the resultant shift of the corresponding Raman band towards higher frequencies [18]. Second, various Si modifications may be formed during SiC synthesis due to temperature variation and pressure [19]. In addition, it has been shown in [20, 21] that electron Raman bands related to nitrogen impurity in SiC may appear in this spectral region. Last, phonon confinement effect must be considered for the nanosized silicon clusters, as this effect causes the band broadening and asymmetry and their shift

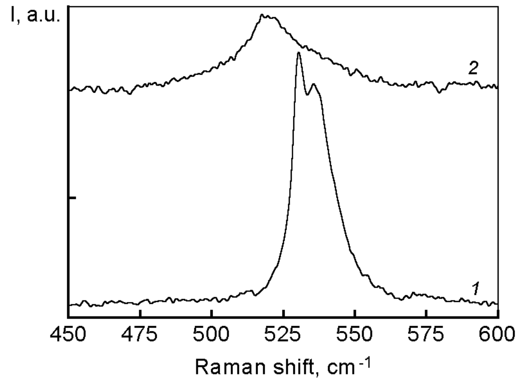

Fig. 5. Raman spectra of bio-SiC derived from hornbeam wood at 2100°C, registered in different geometries: *1*, electrical field vector of exciting laser beam perpendicular to pores axis; *2*, electrical field vector of exciting laser beam along the pores.

to low-frequency side [22]. Let us analyze all the cases in details.

Possible influence of the phonon confinement effect on the Raman band frequency is rather insignificant because majority of the pores in the synthesized bio-SiC is of micrometer size. The probability of electron Raman scattering in our experiment is also low, because, as it is shown in [20, 21], for 6H–SiC highly doped with nitrogen, four characteristic bands at 380, 430, 510 and 638 cm^{-1} are expected, which are not observed in our experimental spectra. Also, the signal from electron Raman scattering is significant only at low temperatures.

The formation of other silicon phases also can be excluded, because those are known to be accompanied by Raman bands at lower frequencies [23] than those observed in our experimental spectra.

In order to study the possible compression of silicon clusters inside pores by SiC matrix, we have measured Raman spectra in two geometries with the electrical field vector of exciting laser beam across and parallel to the pore axis. Fig. 5 shows that for the geometry with the electrical field vector perpendicular to the pore axis, two bands were observed at 529 and 535 cm^{-1} (spectrum *1*). In the case when the electrical field vector is parallel to the pore axis, the Raman spectrum contains only one band at 520 cm^{-1} (spectrum *2*). To explain these differences, we should consider the fact that cooling of the SiC matrix from the synthesis temperature down to room one causes a decrease in linear sizes of both the total matrix and of Si clusters. At temperatures exceeding that of Si liquid → solid transition ($T > 1420°C$), the excess silicon is forced out of the pores due to the matrix open porous structure. At lower temperatures ($T < 1420°C$), the residual silicon is compressed inside the matrix pores because of different thermal expansion coefficients of Si and SiC. In this case, silicon is compressed by SiC matrix only in the plane perpendicular to the pore axis and almost not compressed along it.

It should be noted that the magnitude of the residual silicon clusters compression depends on the SiC matrix synthesis temperature. At synthesis temperature of 1570°C, 3C SiC is formed, while 6H SiC is formed at 2100°C. Unlike cubic 3C polytype, 6H is anisotropic with different thermal expansion coefficients in different directions. Such a difference in SiC matrices results in much greater compression of residual silicon inside the pores in the case of 6H SiC.

The discussed compression of residual silicon in SiC matrix also causes the stresses in the matrix itself. Indeed, TO band in bio-SiC is shifted by ~1 cm^{-1} towards higher frequencies as compared to unstressed bulk SiC samples. The slight shift of this band is explained by lower elastic constants of Si as compared to SiC and by much lower fraction of residual Si compared to SiC volume.

The elastic strain of Si inside the pores can be estimated as follows [24]:

$$\Delta\omega(LO) = \frac{1}{\omega_0}\left(q - \frac{C_{12}}{C_{11}}p\right)\varepsilon_{\parallel},$$

where $\Delta\omega(LO)$ is shift of the bands with regard to their position in unstressed silicon; p and q, optical strain potentials of Si ($p = -1.43\omega_0^2$, $q = -1.89\omega_0^2$); C_{11} and C_{12}, rigidity coefficients of Si; $\varepsilon_{\parallel}$ is the elastic strain in the compression plane. Substitution of the corresponding elastic constants into equation gives $\varepsilon \approx -0.021$, indicating a large compressive stress in the residual silicon inside the pores.

4. Conclusions

The biomorphic SiC ceramics obtained by forced infiltration of carbon matrixes derived from hardwood precursors with liquid silicon has been studied. It is demonstrated that the phase composition of the ceramics obtained depends on the mass ratio of the initial Si and carbon components (ψ). It is found that at $\psi \le 2.33$, relatively low synthesis temperature ($T_{max} \le 1500^\circ C$) and short synthesis time, carbon clusters are present in the ceramics structure. However, at $\psi \ge 2.33$, the residual carbon clusters undetectable by traditional Raman spectroscopy were also revealed by the use of surface enhancement effect which is attained by immersion plating of silver film on the bio-SiC surface. At $\psi \ge 2.33$, Raman bands in Si–Si vibrations region (520–540 cm^{-1}) appear due to residual silicon inside the SiC pores. A high compressive stress causes a shift of these bands towards high-frequency region and TO-LO split in F_{2g} optical mode of the Brillouin zone center. It is found that at synthesis temperatures $T_{max} \sim 1550^\circ C$, 3C polytype is formed. The synthesis temperature elevation up to 1800°C causes formation of both 3C and 6H SiC. A further temperature increase up to $T_{max} = 2100^\circ C$ results in increase of 6H polytype fraction. Thus, the polytype and component composition of the synthesized SiC ceramics can be controlled by varying the synthesis temperature and mass ratio of the initial Si and carbon components.

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Синтез, морфологічні і структурні властивості біо-SiC кераміки

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Досліджено біоморфну SiC кераміку, виготовлену методом примусового просочування рідким кремнієм вуглецевих матриць, одержаних із натуральної деревини твердих порід. Виявлено, що фазовий склад кераміки залежить від масового співвідношення вихідних компонент кремнію та вуглецю, температури та тривалості синтезу. Дослідження за допомогою спектроскопії комбінаційного розсіювання показало, що політип 3C утворюється за температури ~1550°C, при збільшенні температури до 1800°C утворюються обидва політипи 3C та 6H SiC. Подальше підвищення температури до 2100°C збільшує частку 6H політипу. Також виявлено наявність залишкового кремнію всередині пор SiC. Аналіз параметрів фононних ліній дозволив встановити, що залишковий кремній знаходиться під значним напруженням стиску. Використання ефекту поверхневого підсилення інтенсивності КРС дозволило виявити кластери залишкового вуглецю у біо-SiC.