Anisotropy of electric resistivity of Sapele-based biomorphic SiC/Si composites

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Electrical resistivity of Sapele-based biomorphic SiC/Si materials was measured in a wide temperature range from 10 K to room temperature. The samples were fabricated by the reactive infiltration of molten silicon into a carbonized Sapele (African Entandrophragma Cylindricum) wood preform. All the studied samples contained residual Si (10−35 wt.%). It was found that the resistivity–temperature ($\rho(T)$) dependences have semi-metallic behavior which becomes very close to linear metallic one at $100 < T < 300$ K. The obtained values of resistivity were quite low ($\rho \approx 0.002-0.02\,\Omega \cdot$ cm) and showed strong anisotropy: the resistivity along the wood growth axis was several times lower compared with one in the perpendicular direction. The extent of this anisotropy was in a correlation with the amount of residual Si (hence, with the amount of the residual porosity) in a sample. The resistivity perpendicular to the wood growth axis drastically increased with the Si content, whereas the resistivity parallel to it did not depend practically on the Si content. It is suggested that presence of residual carbon in the samples and carrier scattering at SiC/Si interphases could determine the observed character of $\rho(T)$ dependences.

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Wood-based biomorphic SiC (bioSiC) materials have been a matter of interest in the last decade [1–7]. This biomorphic SiC is fabricated by the reactive infiltration of molten silicon into a porous preform of carbonized wood [1–3,5,7]. The final product has a cellular structure of SiC with elongated silicon „channels“. Some residual carbon and empty pores are also present in more or less amounts [4,6]. Moreover, the fine structure of the obtained SiC phase is not uniform throughout a sample: it could exist in micron sized grains and also in a colonies of nano-sized grains nearby the interfaces with carbon [8,9]. A wide variety of SiC/Si composites can be fabricated by melt Si-infiltration of wood depending of the type of wood and technology conditions.

The bioSiC fabrication technique has several important advantages such as low cost (not requiring high-purity starting powders and very high processing temperatures) and fast fabrication (by using an open-cell porous carbon template) [8].

BioSiC ceramics have shown already outstanding mechanical properties when compared to other porous or siliconized SiC [10], which found some different applications. For example, bioSiC ceramics have been successfully developed as reinforcements on refractory concrete [9]. They are also considered to be promising materials for dental and orthopaedic implants [11]. However, physical properties of these materials have not been studied, in detail.

At present there are some different kinds of performance SiC materials, such as chemically deposited (CDV) SiC and Black SiC ceramics which are specially important for their application at high temperature in corrosive environments [12]. Such materials are available in various resistance from conducting to insulating. The conducting type is used as heater elements because of its excellent thermal characteristics. The insulating type can be used as high-frequency plasma components.

The bioSiC ceramics have a complex structure, hence their electric properties can also differ from the standard performance SiC. We studied resistivity temperature behavior of bioSiC ceramics fabricated from Sapele precursors. The resistivities in the directions parallel and perpendicular to the wood axis are compared.

1. Experimental

The biomorphic SiC was fabricated by the reactive infiltration of molten silicon into a porous preform of carbonized Sapele wood (African Entandrophragma Cylindricum). The infiltration was performed in a vacuum following the conventional procedure for reaction formed SiC described elsewhere [4,13,14]. The fabricated SiC ceramics had a cellular structure of SiC with elongated silicon „channels“ (residual Si remained in the pores) in the axial direction of the original wood. Depending on the weight ratio between the carbonized wood and infiltrating Si piece, it is possible to obtain the final SiC/Si samples with different amount of the residual Si. Three different pieces of bioSiC/Si with different weight ratio between the carbonized wood and infiltrating Si piece were prepared. In a first approximation weight percentage of the residual Si content in each of them was obtained on a basis of weights of initial carbon perform, initial infiltrating Si and the obtained product of Si + SiC. The obtained data are shown in table 1 where the studied compositions are noted as Bio-I, Bio-II and Bio-III.

Table 1. Microstructural characterization of bioSiC Sapele-based ceramics

Sample	Si-content (wt.%)	Si-content (vol.%) (from SE image in SEM)	Si-content (vol.%) (from BSE image in SEM)	Mean diameter of Si-filled pores (μm)	Residual porosity (vol.%)	A–Si/SiC interface specific area (μm^{-1})
Bio-I	32 (> 40% from XRD)	26–39	29	12	4.7–5.5	0.1
Bio-II	23	24	21	10.5	12–13.8	0.07–0.08
Bio-III	23.2	11	10	9	18–21	0.04

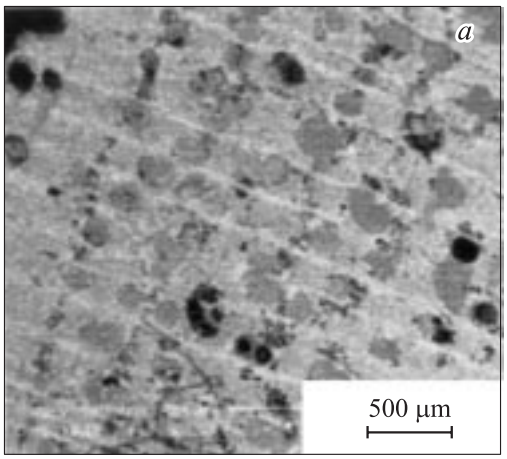
Samples were cut into parallelepipeds with approximate dimensions $1.5 \times 2.5 \times 15$ mm. The electrical resistance–temperature ($R-T$) dependences were measured using the four-probe technique in a wide temperature range from about 10 K to the room temperature. Electric resistivity ρ was calculated without regard for sample residual porosity.

Microstructural observations were performed by optical microscopy and by scanning electron microscopy (SEM) using a Philips XL-30 electron microscopy operating at 30 kV. The volume fraction of the remaining Si in a sample was calculated by topological measurements of SEM images. The topological studies based on the image contrast were completed by analysis of phases in BSE (back scattering electron), allowing a clear distinction between phases.

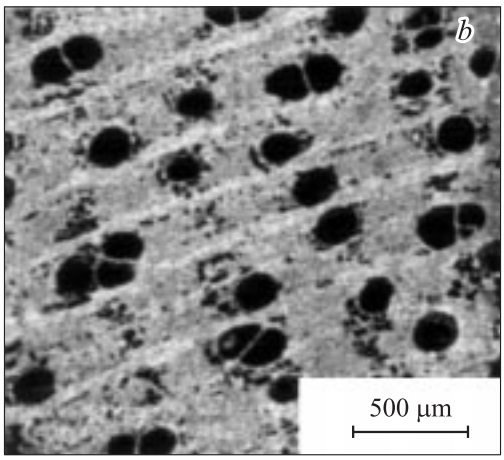
2. Results and discussion

In the table 1 the amount of residual silicon and porosity are presented for all three studied SiC/Si compositions. Weight percentage of Si content estimated on a basis of weight of carbon preform, initial infiltrating Si and the obtained product of Si + SiC is only approximate because the product of such Si infiltration also contains some residual amount of C. In addition, the structure of the fabricated piece of ceramics is not homogeneous due to the nature of wood and additionally non-homogenous distribution of silicon inside the carbon piece during the fabrication process. Surface fraction analysis of SEM images in secondary electrons (SE) and in back scattered electrons (BSE) allowed better estimation of the residual silicon and porosity in each sample. We identified the presence of Si distribution in SE and BSE images in SEM and estimated the volume fraction of silicon and mean diameter of the silicon filled pores and volume portion of the unfilled ones. These data are presented in table 1. From the composition Bio-I to composition Bio-III the amount of residual silicon decreases. This is even evident visually from the SEM micrographs shown in fig. 1, where the structure perpendicular to the wood axis is shown (SiC is round grey phase, residual pores are black).

Fig. 2 shows the $\rho-T$ behavior of the studied compositions in a wide temperature range from about 10 to 300 K. The resistivity was measured in the directions parallel ($\rho_{\|}$) (fig. 2, *a*) and perpendicular ($\rho_{\perp}$) (fig. 2, *b*) to the growth wood axis. As seen, there is pronounced anisotropy of the resistivity for these two directions. Such anisotropy is the largest for Bio-I composition which contains the largest amount of residual Si, hence, lowest content of unfilled pores. Fig. 3 presents the resistivity versus Si content dependence. The resistivity in the direction parallel to the wood axis does not depend on Si content, whereas the resistivity in the perpendicular direction dramatically increases with it.



Bio-I



Bio-III

Figure 1. SEM (in back scattered electrons) micrographs of the as-fabricated materials: Bio-I (*a*), Bio-III (*b*), perpendicular to the wood fibres (Si is round grey phases, empty pores are black).

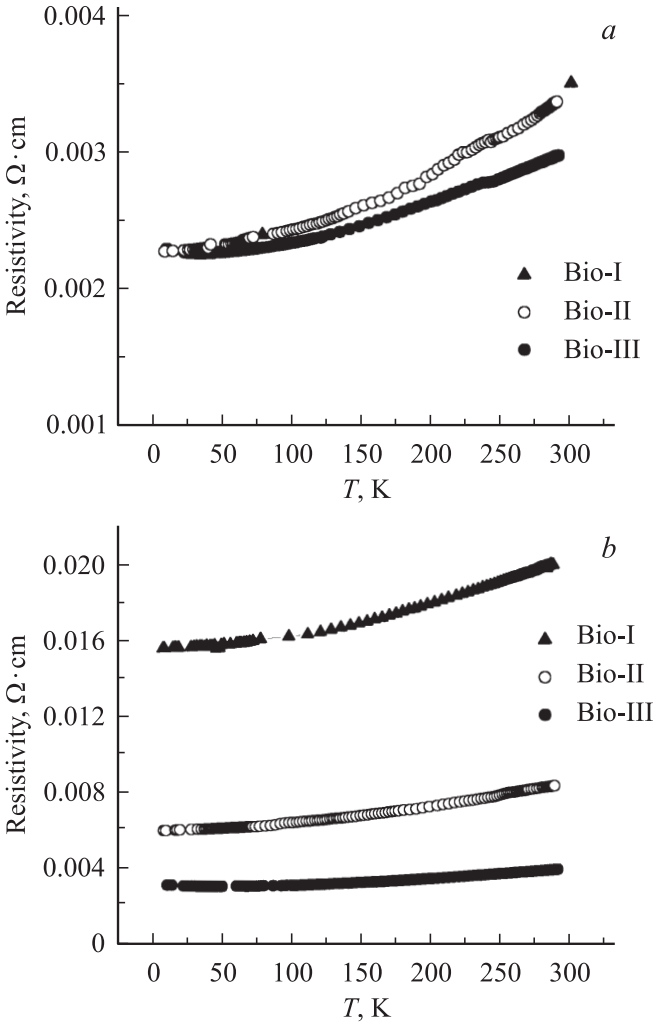


Figure 2. Resistivity versus temperature dependence for the orientation parallel (a) and perpendicular (b) to the growth wood axis.

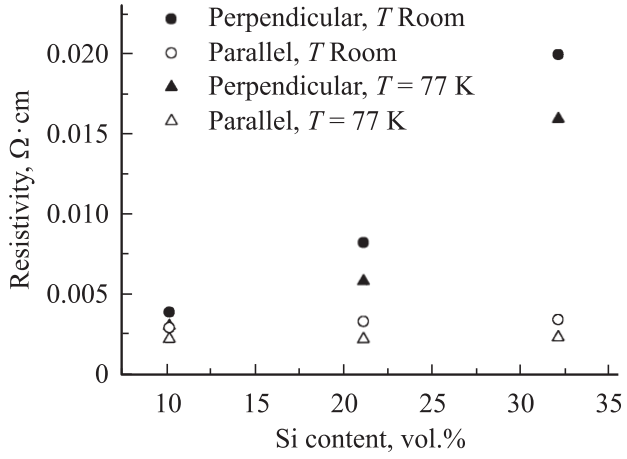


Figure 3. Dependence of resistivity on residual silicon content at 77 K and room temperature for the samples orientations parallel and perpendicular to the pore „channels“ in the initial wood.

The dependence of the resistivity on the temperature for these ceramics shows a semi-metallic behavior, dependences are not completely linear. The resistivity at room T (table 2) is quite low and about one order lower (in the case of the highest $\rho_\perp$ value for Bio-I) compared with the average data for β-SiC single crystals in the literature [15]. However, some special SiC materials with comparable low electrical resistivity are known in literature. These are Black SiC ceramics [12] and a siliconized SiC on the base of carbon fibres in a textile preform [16].

Table 2. Electrical resistivity of bioSiC ceramics on the base of Sapele

Ceramics	ρ at T_{Room} ($\Omega \cdot$ cm)	$\rho_\perp/\rho_\parallel$ at T_{Room}	ρ at 10 K ($\Omega \cdot$ cm)	$\rho_\perp/\rho_\parallel$ at 10 K
Bio-I	$\rho_\perp - 0.02$ $\rho_\parallel - 0.0035$	5.7	$\rho_\perp - 0.016$ $\rho_\parallel - 0.0024$	6.7
Bio-II	$\rho_\perp - 0.0083$ $\rho_\parallel - 0.0034$	2.5	$\rho_\perp - 0.0059$ $\rho_\parallel - 0.0023$	2.6
Bio-III	$\rho_\perp - 0.00395$ $\rho_\parallel - 0.003$	1.33	$\rho_\perp - 0.0031$ $\rho_\parallel - 0.0023$	1.35

$\rho_\perp$ — resistivity in the direction perpendicular to the growth wood axis, $\rho_\parallel$ — resistivity in the direction parallel to it.

The observed anisotropy in the electric conductivity can be associated with the scattering of carriers on the SiC/Si interfaces when the current passes across them, i. e. in perpendicular direction to the wood axis. We made an estimation of the summary interface area A between Si and SiC per the unit volume for the studied sample. Then parameter A is calculated as follows:

$$A = 2\frac{k}{R}, \qquad (1)$$

where k is volume fraction (vol.%) of pores occupied by the residual Si and R is the mean radius of such pores. The obtained values of the A-parameter are presented in table 1. The Bio-I composition has the highest value of A. There is an apparent correlation between the extent of anisotropy and the value of A-parameter: the higher the A-parameter value the higher the anisotropy.

In biomorphic SiC materials, there is always some amount of residual carbon [6]. The amount of residual carbon also seems to be in correlation with residual amount of Si, hence, of empty pores after the infiltration. Less amount of the residual porosity will be most probably in the samples with more completed reaction between Si and C during the infiltration. Carbon most likely participates in electric transport in bioSiC ceramics providing metallic behaviour. However, what is the type of carriers responsible for the conductivity in these ceramics — this question remains still open and required additional investigation.

Thus, it was found that electric transport properties of BioSiC/Si (Sapele-based) are anisotropic in a wide temperature range from 10 K to the room temperature. The value of

this anisotropy depends of the Si-content in the sample and, hence, on the residual porosity. The resistivity perpendicular to the wood axis drastically increased with Si content (and with decrease in the residual porosity), whereas the resistivity parallel to the wood axis did not show a strong dependence with unreacted Si content, remaining about the same for the variation of Si from 10 to 35 vol.%. The $\rho(T)$ dependences ashowed the character of semi-metallic behavior.

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