

PACS 72.20.Pa, 77.84.Bw

Effect of macrostructure on the thermoelectric properties of biomorphous SiC/Si ceramics

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Abstract. In this work, effect of porous macrostructure on the thermoelectric properties of biomorphous SiC/Si ceramics prepared by the liquid silicon infiltration process has been investigated. Temperature dependences of the conductivity and thermal e.m.f. have been measured within the range 20–700 °C. It has been shown that electrical resistivity of the samples decreases drastically as temperature increases over the entire temperature range, indicating semiconductor behavior. All the samples demonstrate a negative thermal e.m.f. confirming the electronic mechanism of charge transfer. It is ascertained that anisotropy of porous macrostructure of the ceramics influences considerably on their electric and thermoelectric properties. The figure of merit maximum value of $1.2 \times 10^{-5} \text{ K}^{-1}$ at 700 °C was obtained.

Keywords: biomorphous SiC ceramics, thermoelectric properties, electrical conductivity, macrostructure.

Manuscript received 02.12.08; accepted for publication 18.12.09; published online 02.03.09.

1. Introduction

The thermoelectric effect that offers a technology providing direct conversion of thermal energy to electricity is of great scientific and technological interest. Thermoelectric converters ensure an ecological process for power generation without pollution of the environment. To obtain materials possessing improved thermoelectric characteristics, intensive investigations of heavily doped semiconductors, advanced alloys and low dimensional structures are performed. Recently, thermoelectric materials, like BiTe [1, 2], PbTe [3], SiGe [4], etc., having satisfactory parameters have been manufactured.

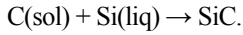
It is known that porous ceramics based on silicon carbide is characterized by a set of attractive properties, namely: mechanical strength, corrosion and oxidation resistance, low specific weight, large surface area ($\approx 1000 \text{ m}^2 \text{ g}^{-1}$), as well as resistance to thermal shocks should be noted. Recently, the reports concerning promising thermoelectric characteristics of SiC based porous ceramics have been appeared [5-9]. One of the methods for obtaining porous SiC/Si ceramics is the steeping of carbon matrix by liquid silicon. Variety kinds of wood subjected to pyrolysis were used as carbon based matrix. This material is called as biomorphous ceramics. It should be noted that carbon

based matrix made from wood corresponds to the material with open porosity that provides the possibility for their steeping by silicon. Moreover, the wood has strong anisotropy of properties due to complex structure. The fact can affect on electric and thermoelectric properties of porous biomorphous SiC/Si ceramics. In this work, the influence of porous macrostructure on the thermoelectric properties of biomorphous SiC ceramics is investigated.

2. Porous SiC ceramics growth technology

The steeping of carbon matrix by liquid silicon, the so-called liquid silicon infiltration process (LSI-process), was used to obtain porous SiC/Si ceramics [10-13]. The LSI-process is based on the impregnation of porous carbon templates by molten silicon and its reaction to silicon carbide. The Persian Walnut (*Juglans regia*), beech (*Fagus sylvatica*), alder (*Alnus glutinosa*), European Hornbeam (*Carpinus betulus*), and pear tree (*Pyrus domestica*) available in Ukraine with average dimensions of 30 mm in diameter and height of 45 mm were used as the biological template in this study. At the initial stage, wood samples were pyrolyzed at 900 °C in an argon atmosphere. After pyrolysis, the carbon templates were reacted with liquid silicon produced by melting Si powder at 1600-1900 °C in a graphite

crucible in inert (Ar) atmosphere. The weight ratio of Si/C was equal to 2.5-3.5. Liquid silicon penetrated through porous medium into matrix. As a result, fusion reaction has been realized



To control the silicon infiltration process as well as the fusion reaction, some of technology stages were carried out in vacuum or in helium atmosphere. In the case of need, residual carbon was removed by firing in oxygen atmosphere at 800-900 °C.

3. Results and discussion

The standard technique of optical and scanning electron microscopy was used to study the structure of ceramics. The stationary method was used to measure the thermo-e.m.f. The samples were prepared in the form of parallelepiped or cylinder. The electric conductivity and Seebeck coefficient were measured in air under different orientations of the samples with respect to the wood growth axis. The sample temperature was controlled by an alumel-chromel thermocouple. The electric contacts were fabricated by deposition of Ti+Ni or by baking of powder mixture of W+Ni.

The view of ceramics' surface in cross-section perpendicular to the wood growth axis is shown in Fig. 1. The peculiarities of the wood structure allow

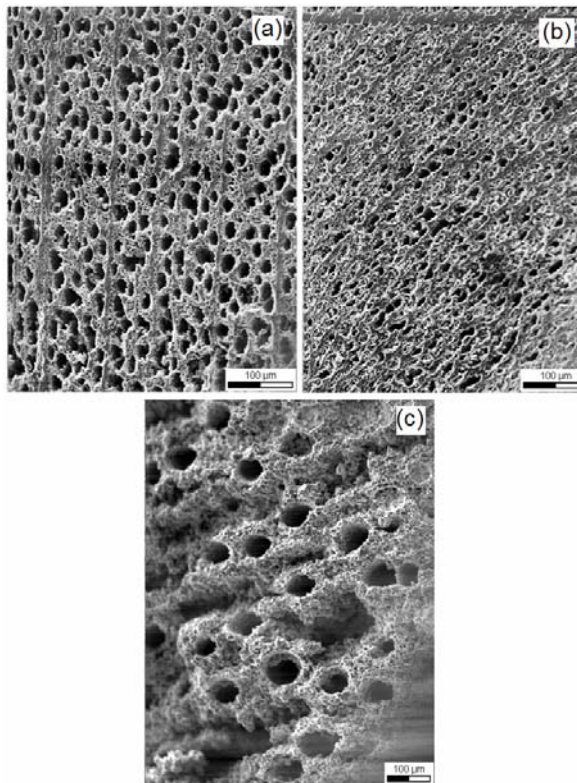


Fig. 1. SEM views of surface of the biomorphous-SiC ceramics fabricated from different kinds of wood: (a) – beech, (b) – pear tree and (c) – Persian Walnut.

fabrication of porous ceramics with different orientations corresponding to the growth direction and annual layers. Two sets of samples have been studied. As it is seen from Fig. 2, in the samples of type-I the electric current direction coincides with the wood growth axis, while in the samples of type-II the current flows perpendicular to the growth direction and annual layers. The samples of type-II are characterized by existence of periodic layers with repetition equal to the size of annual layers. The number of periodic layers θ depends on the kind of wood and geometry of a sample.

The resistivity of SiC ceramics decreases considerably as temperature increases over the entire temperature range measured, which is typical for semiconductors. Besides, it is seen in Fig. 3 that biomorphous SiC/Si ceramics demonstrates essential anisotropy of electric properties. The ratio of specific resistivity for the samples of both types $\rho_{(II-type)}/\rho_{(I-type)}$ depends on θ value and can approach the amplitude up to 10.

Fig. 4 illustrates the influence of macrostructure on the thermo-e.m.f. for biomorphous SiC/Si ceramics fabricated from different kinds of wood. The Seebeck coefficient, α , in all the samples has a negative value that corresponds to the electronic mechanism of charge transfer. The absolute value of α increases with elevating temperature and demonstrates a certain correlation with the structure of SiC ceramics. For example, as can be seen from Fig. 5, increase of the number of layers θ brings the increase of the Seebeck coefficient. The highest magnitude of α observed in some samples approached the value of $-200 \mu V \cdot K^{-1}$.

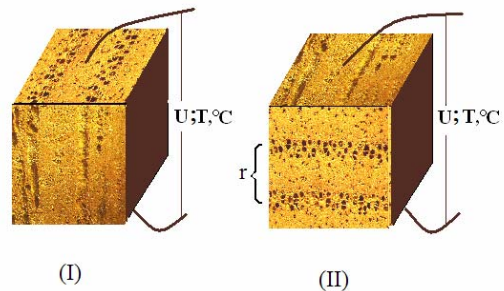


Fig. 2. Schematic view of the bio-SiC thermoelectric converters: (I) – electric current direction coincides with the wood growth axis; (II) – the current flows perpendicular to growth direction and annual layers; r – thickness of the wood annual layer.

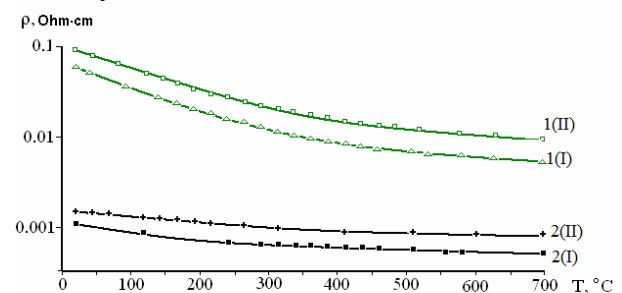


Fig. 3. Temperature dependence of specific resistivity for ceramics fabricated from beech (I) and pear tree (2).

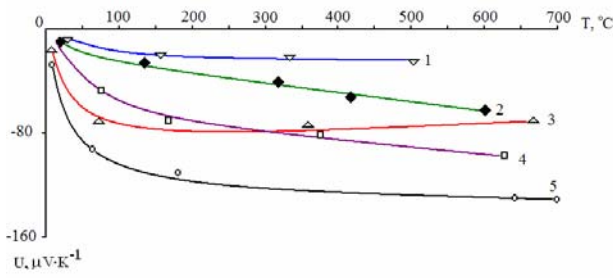


Fig. 4. Temperature dependence of the Seebeck coefficient for samples of type-I fabricated from alder (1), European Hornbeam (2), Persian Walnut (3), beech (4), and pear tree (5).

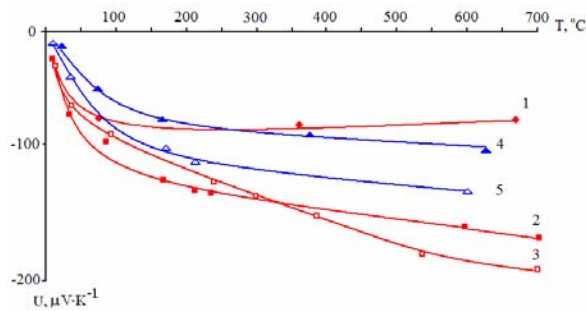


Fig. 5. Temperature dependence of the Seebeck coefficient for samples of type-I and type-II fabricated from Persian Walnut (1 – type-I, 2 – type-II, $\theta = 4$, 3 – type-II, $\theta = 10$) and beech (4 – type-I, 5 – type-II, $\theta = 5$).

The figure of merit of the sample was calculated using the following equation:

$$Z = (\alpha^2/\rho\lambda),$$

where Z is figure of merit (K^{-1}), α is the Seebeck coefficient (V/K), ρ is the specific resistivity (Ohm·m), λ is the thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$). Obviously, the high quality thermoelectric materials should possess a high value of the Seebeck coefficient, low thermal conductivity that must support the temperature gradient and good electric conductivity.

Thermal conductivity is an important factor that will affect the figure of merit. In this connection, porous material has the advantage over the bulk one. Indeed, it is well known that the thermal conductivity of bulk SiC exceeds that of porous SiC by several times.

The data concerning the thermal conductivity of porous SiC ceramics fabricated by different methods are presented in Table.

Table. Thermal conductivity of SiC ceramics.

Growth technology and composition	$\lambda, W \cdot m^{-1} \cdot K^{-1}, T = 600 \text{ }^\circ\text{C}$	Reference
Porous SiC/C composite made from a mixed powder of wood charcoal and SiO ₂	4-25	[7]
Synthesis from SiC and Si powders	20	[8]
Composite SiC+(15 % Si)	22.7	[9]

It is seen that the thermal conductivity of porous SiC ceramics fabricated by different methods varies from 4 to 25 $W \cdot m^{-1} \cdot K^{-1}$ at $T = 600 \text{ }^\circ\text{C}$. These values were used to estimate the figure of merit for biomorphous SiC ceramics. The samples of type-I fabricated from pear tree wood showed the best results. Due to the low specific resistivity ($\rho < 4 \times 10^{-4} \text{ Ohm} \cdot \text{m}$) and high value of the Seebeck coefficient ($\alpha > 140 \text{ V/K}$), the figure of merit for these samples approaches the value of $1.2 \times 10^{-5} K^{-1}$ at $700 \text{ }^\circ\text{C}$, which is in good agreement with data obtained in Ref. [7].

4. Conclusions

Study of structure, electric and thermoelectric characteristics of biomorphous SiC/Si ceramics grown using the liquid silicon infiltration process has been carried out. It is observed that the electrical resistivity of SiC ceramics decreases considerably as temperature increases over the entire temperature range measured, which is indicative of semiconductor behavior. All the samples demonstrate a negative thermal e.m.f. confirming the electronic mechanism of charge transfer. The absolute value of α increases with elevating temperature and demonstrates a certain correlation with the structure of SiC ceramics. It has been shown that efficiency of thermoelectric conversion in biomorphous SiC/Si ceramics increases with temperature rise. The samples of SiC ceramics of type-I demonstrate the highest values of the figure of merit. According to our estimation, the figure of merit for these samples approaches the value of $1.2 \times 10^{-5} K^{-1}$ at $700 \text{ }^\circ\text{C}$. We suppose that optimization of 3D macroporous structure of the biomorphous ceramics as well as enhancement of electric conductivity by doping should improve thermoelectric properties of SiC materials.

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