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Effect of Si Infiltration Method on the Biomorphous SiC Microstructure Properties

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Two types of wood-based biomorphous SiC composites with different microstructure are obtained by infiltration of carbon template with liquid or vapour silicon. The oak, pine, lilac, walnut, acacia woods available in Ukraine are used as the biological template in this work. The SEM, optical and EPR data indicate that biomorphous SiC obtained by melt infiltration consists of crystalline 3C-SiC phase while that obtained by vapour infiltration consists of both crystalline and amorphous 3C-SiC phase.

Були одержані два типи деревного біоморфного SiC-композиту з різною мікроструктурою просочення вуглецевого шаблону газоподібним або рідким кремнієм. Деревина дуба, сосни, бузку, волоського горіха, акації, які поширені в Україні, використовувалися як біологічний шаблон у цій роботі. Дані оптичні, СЕМ і ЕПР показали, що одержані просоченням розтопом біоморфні композити SiC складаються із кристалічної й аморфної фаз 3C-SiC.

Были получены два типа древесного биоморфного SiC-композита с различной микроструктурой пропитки углеродистого шаблона газообразным или жидким кремнием. Древесина дуба, сосны, сирени, грецкого ореха, акации, распространенные в Украине, использовались как биологический шаблон в этой работе. Данные оптические, СЭМ и ЭПР показали, что полученные пропиткой расплавом биоморфные композиты SiC состоят из кристаллической и аморфной фаз 3C-SiC.

Key words: biomorphous SiC/Si composites, SEM, Raman spectroscopy, EPR.

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1. INTRODUCTION

Biomorphous composites SiC/Si are known in the literature as ecoceramics—environment conscious ceramics [1–3]. Among the biomorphous composites, the porous SiC ceramics has been considered to be one of the best candidate materials for orthopaedic and dental implants due to their high level of biocompatibility, chemical inertness and mechanical strength [4–6]. Porous SiC has also a great potential for many industrial applications such as light ultra strong material in aerospace and motorcar industry, and as well as a heat insulation material due to its low thermal expansion coefficient, small value of the relative density, mechanical strength, high chemical inertness, oxidation and corrosion resistance.

The objective of the present work is to examine the effect of infiltration method on the parameters of wood-based biomorphous SiC composite. For this purpose, the biomorphous SiC was fabricated by infiltration of the carbon template with liquid or vapour silicon (Si).

2. PREPARATION TECHNOLOGY

The technology process of biomorphous SiC preparation is well known [1–3]. The developed processing scheme for manufacturing of wood-based biomorphous SiC composite by infiltration method used in this work is shown in Fig. 1.

Oak, pine, lilac, walnut, acacia woods available in Ukraine with average dimensions of 20–40 mm in diameter and height of 12 mm were used as the biological templates in this study. At initial stage, wood samples were pyrolized at 900°C in argon atmosphere. After pyrolysis, the carbon templates were reacted with liquid Si produced by melting Si powder at 1500°C in graphite crucible in inert (Ar) atmosphere. For this purpose, the resistive furnace (REDMET 30) with graphite crucible was used. The carbon templates were placed into the graphite crucible together with well-milled Si. The C/Si ratio was of 1/2. Design of the graphite crucible allows fixing the position of the carbon templates so that only half of the carbon template was immersed into the Si melt providing the infiltration of that with both liquid and vapour Si.

The spontaneous Si infiltration of the carbon templates was performed at 1500–1600°C during 60–120 min in inert atmosphere (Ar or He). After that, the temperature was raised up to 1800–1900°C and held for 30–60 min. During this synthesis and unreacted Si evaporation occurred.

The final material of the reaction was a Si/C composite with a wood-like microstructure. An excess carbon was burn out in furnace in oxygen atmosphere at 900°C for 2 hours.

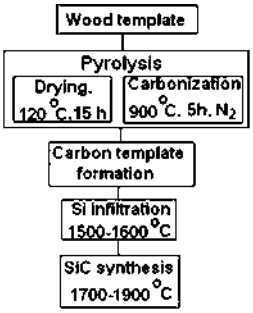


Fig. 1. Processing scheme for fabrication of biomorphous SiC.

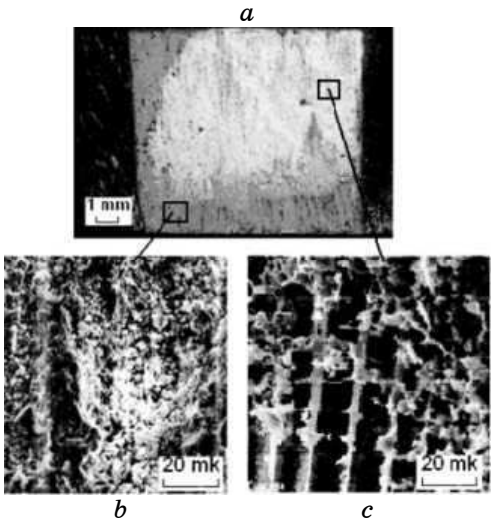


Fig. 2. Photo (*a*) and SEM images (*b*, *c*) of the transverse section of biomorphous SiC grown from walnut.

3. EXPERIMENTAL RESULTS AND DISCUSSION

Optical and scanning electron microscopy (SEM), atomic force microscopy, Raman scattering spectroscopy and electron paramagnetic resonance (EPR) were used for compositional and structural analysis of biomorphous SiC.

Surface and transverse cross section of the template were studied by SEM after infiltration and carbonizations. Figure 2 shows images of the transverse cross section of biomorphous SiC grown of walnut.

It was established that the mechanical properties, structure and colour of biomorphous SiC depend on the carbon template infiltration method. The melt infiltration resulted in final material with high me-

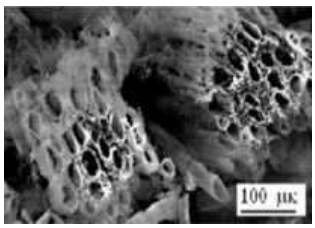
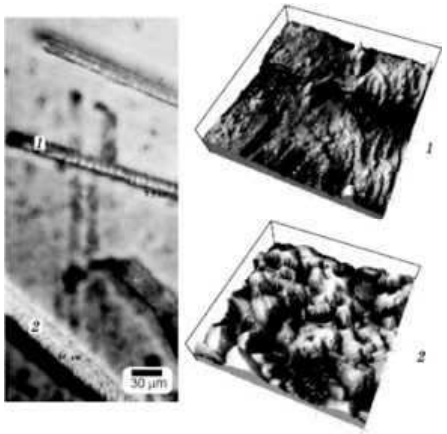


Fig. 3. Optical microscopy image of tubular fibre packages of the biomorphous SiC grown from lilac.



a *b*

Fig. 4. Photomicrography (*a*) and AFM image (*b*) of SiC fibres grown from pine with scan size of 4×4 μm and *Z*-range of 0.1 μm.

chanical strength and green-brown colour which was labelled as SiC-1 (see Fig. 2, *b*), while the infiltration with Si vapour resulted in final material of white colour with fibrous structure and was labelled as SiC-2 (see Fig. 2, *c*). It was found also that type of infiltration (with liquid or vapour Si) depends on wood species. The template prepared from pine and lilac wood were infiltrated only by vapour Si while the templates prepared from walnut, oak, ash tree, and pear were mainly infiltrated with liquid Si. This was possibly caused by the different porosity and molecular properties of the carbon template surface prepared from the wood of various species. The fibrous structure of SiC-2 was clearly demonstrated when excess carbon was burn out. The fibre diameter is determined by tubular pore sizes in carbon template and varies from 1 to 30 micron. The fibres have a low mechanical strength and could be easy separated from the carbon template walls.

As it is seen from Figs. 3 and 4, the fibres have flaked structure and ultrasonic treatment easy separates the flakes.

Raman spectra (RS) were taken by double grating spectrometer DFS-24 at room temperature. The 514.5 nm line of an Ar^+ laser was used for the excitation. The signal was registered with cooled phototube working in photon counting mode in back scattering geometry.

Figure 5 shows RS observed in two types biomorphous SiC grown from lilac. Analysis of RS peak frequencies observed in biomorphous SiC shows that biomorphous SiC-1 should be attributed to the 3C polytype. Slightly higher values of LO and TO phonon bands (TO—796 cm^{-1} and LO—972 cm^{-1}) with respect to those in crystalline 3C SiC indicate that the biomorphous SiC is affected by compression. The LO and TO phonon bands in RS of SiC-2 have lower intensities than in SiC-1. In addition, a broad band centred at 765 cm^{-1} was observed in RS of SiC-2 and could be attributed to the amorphous phase of SiC [7, 8]. Thus, SiC-2 consists of crystalline and amorphous phase of 3C SiC. It should be noted that depending on the SiC technology treatment the disordered (*D*) and graphitic (*G*) bands were observed in RS of SiC-1 (see Fig. 5, *b*) due to clusters of carbon spots [9] which disappeared when excess carbon was burn out.

EPR spectrum taken on biomorphous SiC-2 at 77 K and 9 GHz is shown in Fig. 6. The biomorphous SiC-2 under EPR investigation was preliminary annealed in oxygen atmosphere at 900°C to remove the excess carbon.

EPR spectrum consists of single intense line with isotropic *g*-factor $g = 2.0023$ and width of 0.3 mT, which could be assigned to the carbon dangling bonds in 3C SiC [10]. The EPR signal from carbon clusters was not observed.

Figure 2 shows that 3C SiC grains of 5–10 μm size were formed in the case of melt infiltration. This conclusion is confirmed by results obtained in [11]. Therefore, it could be suggested that formation of the SiC and SiC precipitates are caused by process of carbon dissolution in liquid Si (model via solution-precipitation) [12, 13]. The infiltration with vapour Si resulted in smooth-faced, unstructured fibres consisting of amorphous SiC possibly due to diffusion-controlled process [14–16].

4. SUMMARY

The growth technology and parameters of wood-based biomorphous SiC ceramics obtained by infiltration with liquid or vapour silicon were examined. The relationship between infiltration method and microstructure of biomorphous SiC was established. It was found that structure and phase composition of the material depend on the carbon template infiltration method. Optical and SEM data indicate that the melt infiltration results in biomorphous SiC with crystalline phase of 3C SiC with the faceted morphology while the infiltration with Si vapour results in SiC with fibrous structure consists of both crystalline and

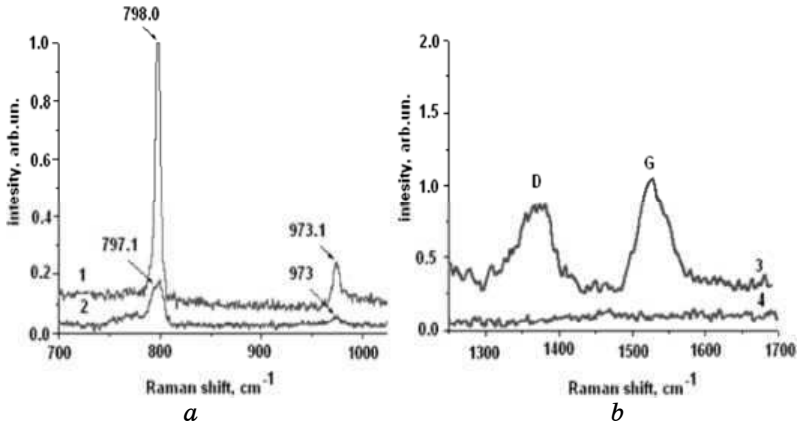


Fig. 5. RS of SiC-1 and SiC-2: *a*—RS of SiC observed in the C–C oscillation range, *1*—SiC-1, *2*—SiC-2; *b*—RS of SiC-1 observed in the 1300–1700 cm^{-1} range, *3*—as synthesized SiC-1, *4*—carbon excess was burn out from SiC-1.

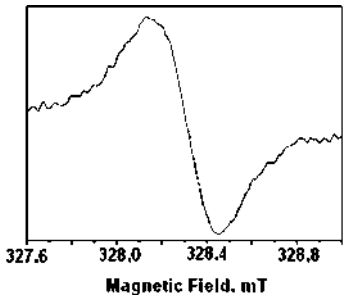


Fig. 6. EPR spectrum recorded at 9 GHz and 77 K in biomorphous SiC-2.

amorphous phases of 3C SiC. Thus, it was suggested that SiC mechanism formation is governed by infiltration method.

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