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ScienceDirect
Journal of the European Ceramic Society 31 (2011) 1317–1323
www.elsevier.com/locate/jeurceramsoc

Electrical properties of biomorphic SiC ceramics and SiC/Si composites fabricated from medium density fiberboard

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Available online 31 July 2010

Abstract

A study has been made of the dependences of the electrical resistivity and the Hall coefficient on the temperature in the range 1.8–1300 K and on magnetic fields of up to 28 kOe for the biomorphic SiC/Si (MDF-SiC/Si) composite and biomorphic porous SiC (MDF-SiC) based upon artificial cellulosic precursor (MDF – medium density fiberboards). It has been shown that electric transport in MDF-SiC is effected by carriers of *n*-type with a high concentration of $\sim 10^{20}$ cm^{-3} and a low mobility of ~ 0.4 cm^2 V^{-1} s^{-1}. The specific features in the conductivity of MDF-SiC are explained by quantum effects arising in disordered systems and requiring quantum corrections to conductivity. The TEM studies confirmed the presence of disordering structural features (nanocrystalline regions) in MDF-SiC. The conductivity of MDF-SiC/Si composite originates primarily from Si component in the temperature range 1.8–500 K and since $\sim$500 to 600 K the contribution of MDF-SiC matrix becomes dominant.

Keywords: C. Electrical properties; Biomorphic SiC; SiC/Si composite; Electron microscopy

1. Introduction

The studies of electrical properties of silicon carbide (SiC) ceramics and SiC-based composites have tremendous scientific significance and practical interest as well. Due to their high performance characteristics at high temperatures and good resistance to corrosive environments the SiC materials are promising to be used for heater elements, resistance thermometers and thermoelectric power generators in space, automotive and energy transformation industries.[1]

The main fabrication processes of SiC ceramics are carbothermic reduction of SiO_2,[2] reactive compaction,[3,4] and hot sintering.[5,6] Recently, natural wood-derived biomorphic SiC (bio-SiC) ceramics have been a matter of interest.[7–14] The processing technique of porous SiC ceramics from wood involves the pyrolysis of natural wood precursors, followed by the infiltration of molten silicon to form silicon carbide (SiC), retaining the initial wood porous structure.[9–14] Some residual Si remains in cellular pores forming thereby SiC/Si composite. The pure porous material, bio-SiC, is produced from the SiC/Si composite by etching silicon out of the channel pores.[15] Both biomorphic SiC/Si composite and porous SiC ceramic (the composite matrix) have highly anisotropic structure, replicating the cellular structure of natural wood (cellular channel pores elongated along the tree growth direction). Some amount of unreacted carbon is also present in biomorphic SiC/Si composite as well as in porous bio-SiC.[13]

The bio-SiC has several advantages over conventional SiC. It presents relatively light material with open porous structure, which possesses excellent mechanical properties in compression and flexure.[16] The technology of its fabrication allows for relatively easy production of complex shapes by using preliminary machining of biomorphic carbon precursor.[12] The processing of bio-SiC is much cheaper because it occurs at temperatures that are much lower than those required for SiC sintering or hot-pressing techniques. The latter requires temperatures exceeding 2000 °C.[4,5] The structure and resulting properties, mechanical ones at least, of bio-SiC and bio-SiC/Si strongly depend on the original wood precursor used.[17]

Investigation of the electrical transport properties of this new class of materials – biomorphic natural wood-derived SiC/Si composites and porous bio-SiC has been recently attracting considerable attention. For example, the electric resistivity ρ of biomorphic SiC/Si composites derived from sapele,[18] white

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0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2010.06.015

eucalyptus[19–21] and beech[22] was measured in the temperature range 5–300 K. In Ref.[23], the temperature range of measurement of the dependence $\rho(T)$ was extended to 950 K for the SiC/Si composites fabricated from white eucalyptus. These studies revealed that the electrical resistivity of biomorphic SiC/Si is anisotropic, i.e. there is a difference between the resistivity ρ_{II} measured along the axial direction (parallel to the tree growth direction) and the resistivity $\rho_{\perp}$ measured along the transverse direction. In the temperature range 4.2–300 K, both temperature dependences $\rho_{\mathrm{II}}(T)$ and $\rho_{\perp}(T)$ follow semimetallic pattern: the electrical resistivity varies insignificantly at low temperatures and increases starting from ~100 K. ρ_{II} of the biomorphic SiC/Si composites at room temperature varies in the range 10^{-3} to $10^{-2}\,\Omega\,\mathrm{cm}$. The conductivity of biomorphic SiC/Si composites (derived from eucalyptus[21] and beech[22]) was found to originate primarily from Si component and to be provided by carries of p-type with concentration of the order of $10^{19}\,\mathrm{cm}^{-3}$ and high mobility (~$10^3\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ at 4.2 K).[22] All kinds of wood taken as initial precursors in the above considered works belong to the wood with open porosity.[24]

However, $\rho(T)$ dependences measured for bamboo wood-derived SiC/Si composite exhibited a semiconducting pattern over a wide temperature range (25–1000 K)[25] that is contrary to metallic $\rho(T)$ behaviour of biomorphic SiC/Si from sapele,[18] eucalyptus[19–21] or beech.[22] This difference seems to be explained by the specificity of bamboo structure. As it was noted in Ref.[24] carbon preforms from bamboo contain a combination of channel pores and closed cells that impede the complete infiltration of Si. As a result interconnecting Si-filled channels network probably is not formed. This can also lead to a large amount of unreacted carbon which can form own conducting percolation paths.

The resistivity of porous bio-SiC (from eucalyptus[21] and beech[22]) at low temperatures (4.2–300 K) is several orders of magnitude higher than the resistivity of the respective SiC/Si composites. The $\rho(T)$ dependences of the bio-SiC demonstrate semiconducting behaviour in the range 4.2–300 K. The electrical transport in beech-derived bio-SiC is effected by n-type carriers with a high concentration of ~$10^{19}\,\mathrm{cm}^{-3}$ and a low mobility of ~$1\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$.[22] It has been concluded[22] that the electrical transport in the natural beech-derived SiC occurs similarly to the transport in strongly disordered semiconductors and could be described with theory of quantum corrections to the conductivity.[26]

Nowadays precursors which could be alternative to the natural wood are considered to be promising for processing bio-SiC and bio-SiC/Si materials. These are artificial compacted fiberboards or, more specifically, medium density fiberboards (MDF). Processing technology of MDF-based biomorphic SiC (MDF-SiC) and respective SiC/Si (MDF-SiC/Si) composite is similar to that used for natural wood precursors.[27,28] The MDF-SiC and MDF-SiC/Si have some advantages compared with similar materials processed from natural wood precursor. Upon carbonization, the homogeneity and consistency of fiberboards result in the formation of a consistent, low-coast hard carbon.[29] Because of better homogeneity carbonized fiberboards can be more easily machined into complicated shapes compared with carbonized woods.[29] Since MDF boards are formed under controlled conditions, MDF-SiC can possess reproducible homogenous structure unlike natural wood-derived SiC materials the structure of which depends on yearly rings, climate factors, etc. Processing of MDF by pressing allows a choice of density and porosity of the precursor that can modify functional characteristics of final MDF-SiC. There are only a few papers devoted to mechanical properties of MDF-SiC and MDF-SiC/Si composites.[27,28] Physical properties, specifically electrical ones, of MDF-SiC have not been studied, at all.

The aim of the present work is to investigate electrical properties of porous bio-SiC ceramic and bio-SiC/Si composites both obtained from MDF precursors. Measurements have been made of temperature dependences of the electrical resistivity, as well as the Hall coefficient in a temperature range of 1.8–300 K and magnetic fields of up to 28 kOe. The type and concentration of carriers in MDF-SiC were determined from measurements of the Hall coefficient. Electrical properties of MDF-SiC/Si and MDF-SiC are compared with those of similar biomorphic materials fabricated from natural wood (eucalyptus, beech, bamboo).

In addition, we also present some of our preliminary data on resistivity-temperature behaviour of MDF-SiC and MDF-SiC/Si materials at elevated temperatures (from 300 to 1300 K).

2. Experimental procedure

Porous biomorphic SiC ceramic and SiC/Si composite, both derived from MDF boards, have been prepared. A commercial medium density (0.6–0.8 g/cm^3) MDF boards were chosen as precursor. The processing technique of MDF-based SiC (hereinafter MDF-SiC) and SiC/Si (MDF-SiC/Si) composites included several stages. The processing technology is presented in details in Refs.[27,28]. Briefly, first a MDF piece of 50 mm × 30 mm × 30 mm was pyrolized at 1050 °C in flowing argon. As a result, the biocarbon preform (MDF-C) was obtained.

Unlike the biocarbon obtained by pyrolysis of the natural wood (eucalyptus, beech, sapele, pine), which has open channel pores along the tree growth direction, the MDF-C has more homogeneous structure.[28] An example of the microstructure of the MDF-C is shown in Fig. 1. Samples of MDF-C were cut with dimensions of 3 mm × 3 mm × 20 mm, the long dimension being perpendicular to the direction of the load application in MDF pressing.

Each sample of MDF-C perform was infiltrated with an excess of Si to the stoichiometric amount needed for all the C amount in the perform. The final SiC/Si composites were formed.

Pure biomorphic MDF-SiC samples derived from MDF boards were obtained by etching silicon away with a mixture of hydrofluoric and nitric acids.[15]

The dependences of electrical resistivity and of the Hall constant R on temperature and magnetic field H were measured by the standard four-probe technique. In these measurements the electric current was passed along the long side of the sample, i.e., perpendicular to the pressing direction in the parent MDF board