SiC Nanorods grown on SiC coated Wood Charcoal

Toshimitsu Hata[1], Sylvie Bonnamy[2], Paul Bronsveld[3], Vinicius Castro[1],
Masashi Fujisawa[1]; Hikari Kikuchi[4]; Yuji Imamura[1]
[1] *Wood Research Institute, Kyoto University, Kyoto 611-0011, Japan*
[2] *CRMD, CNRS-Université, 1B rue de la Férollerie, 45071 Orléans Cedex 2, France*
[3] *Department of Applied Physics, Materials Science Center, Groningen-Netherlands*
[4] *S S Alloy, Kagamiyama, Higashi Hiroshima 739-0046, Japan*

Corresponding author e-mail address: toshi@mbox.kudpc.kyoto-u.ac.jp (T.Hata)

Introduction

Wood charcoal, especially from cedar-based wood, is an interesting material not only for the anisotropic texture of its cell walls and pores but also for the more than reasonable strength exhibited even with a 60% porosity. Unfortunately, charcoal has limited applications above 500 °C due to a decrease in strength and poor oxidation resistance. On the other hand, silicon carbide is a high temperature material with a high compressive strength [1].
In this study we combined the favorable properties of both materials and synthesized a SiC/C composite with, as spin-off, the growth of SiC nanorods.

Experimental

Japanese cedar (*Cryptomeria japonica*) carbonized at 700 °C was vacuum infiltrated with tetraethylorthosilicate (TEOS), resulting in samples saturated with 36% Si-based on the dry charcoal weight. Subsequently, the infiltrated specimens were heated at 1500 °C for 30 min by a pulse current sintering method. The microstructure was investigated using a SEM / FIB dual beam microscope for sample identification and preparation and a TEM microscope for further characterization.

Results and Discussion

Under the conditions set for this experiment, the optimal sintering temperature for β-SiC is 1500^{o}C [2]. At this temperature it is possible to produce about a 1 μm thick SiC layer at the char internal pore surfaces as depicted in the SEM image of Figure 1 showing a cross section obtained with the FIB machining process. Coating and pore walls are ion milled with Ga ions reason why the dimensionality can be very precise. Furthermore, in playing with the experimental conditions, SiC nanorods can be formed, growing randomly in the open pores together with the SiC coating.
The SEM image in Figure 2 shows a few of these SiC nanorods. Their diameter range from 100 to 500 nm and the length varies from 10 to 30 μm only limited by the cell pore size. Occasionally whiskers with a diameter of around 1 μm were found.

The bright field TEM image in Figure 3 (a) shows an example of such an irregular, layer-like grown SiC nanorod formed by the Vapor- Vapor (VV) mechanism [3, 4]. An enlargement of the area indicated by the white box in Figure 3 (a) is shown in Figure 3 (b). Scanning Electron Microscopy images could confirm the presence of a spherical termination usually of a higher diameter than the bamboo-like rods. It is known to consist of a SiC nucleus.
Making use of the diffraction pattern related to the white box in Figure 3 (b) a dark-field TEM image was taken and reproduced in Figure 3 (c). It clearly indicates the (111) preferred growth direction of the SiC nanorod [5]. Needle-like crystals are grown under a supersaturated atmosphere of CO and SiO. SiC nanorods grow when SiO reacts with the carbon of the (111) plane depositing SiC while releasing carbondioxide. The (111) plane of SiC having the lowest energy grows fastest and is, therefore, normal to the axis of the SiC nanorod [6].
A carbon layer was found coating the nanorods as shown in Figure 3 (d). The carbon layer extends along the nanorods and wets the SiC everywhere except near the tip. It is said that carbon coated nanorods are far less susceptible for electron beam damage than uncoated nanorods [7].

Conclusions

Japanese cedar carbonized at 700°C was vacuum infiltrated with tetraethylorthosilicate (TEOS) and heated at 1500 °C for 30 min by electric pulse heating. SEM images of the sample after the FIB machining process revealed 1 μm reaction layer covering the pore walls. Moreover, a large number of nanorods were present inside the pores. TEM characterization confirmed them to be SiC nanorods grown along the (111) direction and coated with a graphitic carbon layer.

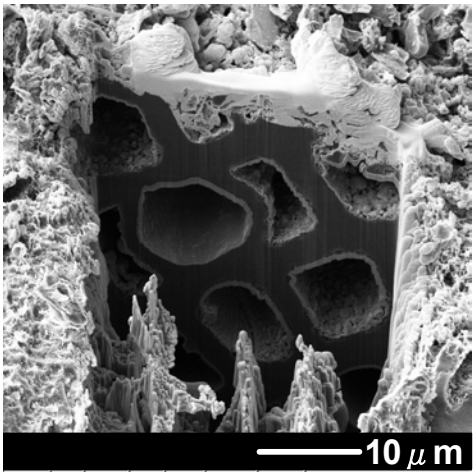

Figure 1. SEM image of FIB machined cross section of wood charcoal showing the pore walls with one micron thick SiC coating.

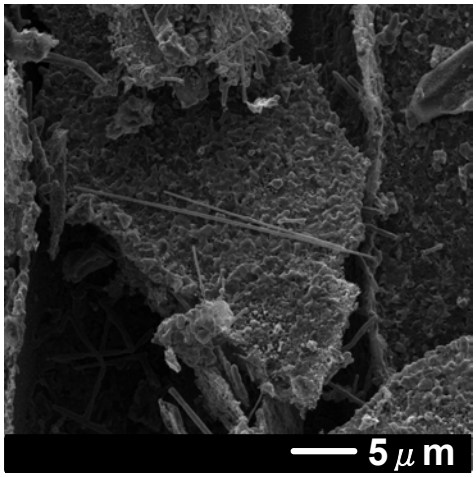

Figure 2. SEM image of the inside of a pore with SiC nanorods hanging above the one micron thick SiC coating of a pore wall in wood charcoal.

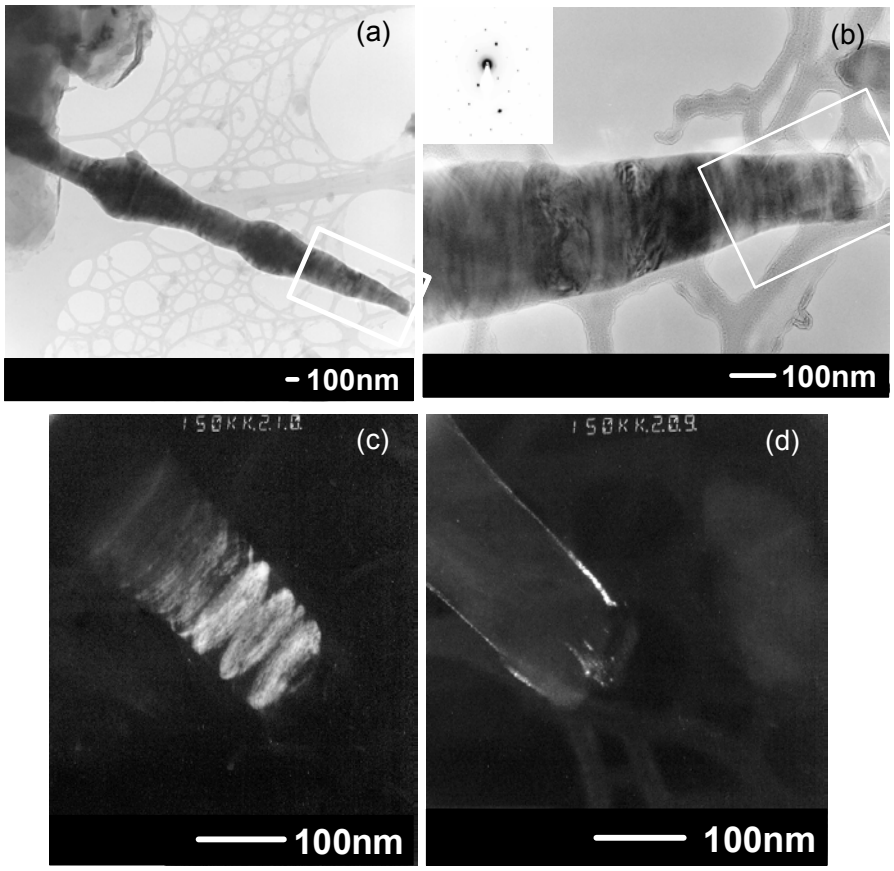

Figure 3. SiC nanorods formed together with silicon carbide coatings on pore walls in wood charcoal. (a) TEM image of bamboo like SiC nanorod. (b) TEM image of white box in (a) with SiC tip nucleus in insert is the diffraction pattern. (c) TEM dark field image of white box in (b) showing the (111) preferred growth direction. (d) TEM 002 dark field image of white box in (b) showing the graphitic carbon layer.

References

[1] Greil P, Lifka T, Kaindl A. Biomorphic cellular silicon carbide ceramics from wood: I. Processing and microstructure. J.Eur.Ceram.Soc. 1998;18:1961-1973.
[2] Castro V, Fujisawa M, Hata T, Bronsveld P, Vystavel T, De Hosson J, Kikuchi H, Imamura Y. Silicon carbide nanorods and ceramics from wood, Key Eng. Mat. (in print).
[3] Gao YH, Bando Y, Kurashima K, Sato T. The micro structural analysis of SiC nanorods synthesized through carbothermal reduction. Scripta materialia 2001;44:1941-1944.
[4] Zhou D, Supapan S. Production of silicon carbide whiskers from carbon nanoclusters, Chem. Phys. Let. 1994;222:233-238.
[5] Xu H, Bhatia T, Deshpande SA, Padture NP. Microstructural evolution in liquid-phase-sintered SiC: Part **I**, effect of starting powder, J.Am.Ceram.Soc. 2001;84:1578-1584.
[6] Gao YH, Bando Y, Kurashima K, Sato T. SiC Nanorods prepared from SiO and activated carbon, J.Mat.Sci.2002;37:2023-2029.
[7] Han W, Zettl A. An efficient route to graphitic carbon layer-coated gallium nitride Nanorods, Advanced materials 2002;14(21):1560-1562.