Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of the European Ceramic Society 26 (2006) 719–723
www.elsevier.com/locate/jeurceramsoc

Comparison between carbonization of wood charcoal with Al-triisopropoxide and alumina

Paul Bronsveld[a,*], Toshimitsu Hata[b], Tomas Vystavel[a], Jeff DeHosson[a], Hikari Kikuchi[c], Koei Nishimiya[d], Yuji Imamura[b]

[a] Department of Applied Physics, Materials Science Centre, University of Groningen, Groningen 9747 AG, The Netherlands
[b] Research Institute for Sustainable Humanosphere, Kyoto University, Uji, Kyoto 611-0011, Japan
[c] S S Alloy, Techno plaza 308, 3-13-26 Kagamiyama, Higashi Hiroshima, Hiroshima 739-0046, Japan
[d] Hokkaido Forest Products Research Institute, Hokkaido 071-0198, Japan

Abstract

A comparison was made between the catalytic carbonization of biomass carbon suspended in Al-triisopropoxide and in biomass carbon mixed with 40 μm sized Al_2O_3 particles. Both types of samples were plasma sintered during 5 min under an argon pressure of 50 MPa at temperatures up to 2200 °C. Plate-like catalytic graphitization develops by formation and dissociation of plate-like Al_4C_3. Plasma sintering under the proper CO partial pressure and heat treatment temperature is instrumental in forcing the Al_2O_3 to react with the carbon, forming first Al_4C_3 and subsequently graphite. The difference between Al-triisopropoxide and Al_2O_3 is a matter of intensity of the graphite reaction versus the size of the graphite patches.

Keywords: Graphitisation; Sintering

1. Introduction

Currently, carbonized materials from wood or waste wood have been focused upon as raw materials for carbons. These carbons are important for the production of artificial graphite. Wood charcoal transforms into graphite at temperatures around 2200 °C rather easily.[1] The well-known structure of merging and interlinking of fibrils was observed preferentially at these higher heat treatment temperatures. At the lower temperatures onion like structures were observed consisting of concentric rings of (0 0 0 2) graphite layers, a distance of 0.34 nm apart. The process of catalytic graphitization of ungraphitized carbon has been extensively studied.[2–4] In the presence of catalysts such as Fe, Co and Ni, the graphitization accelerates and runs at a lower temperature, in the case of solid phase graphitization even below 1000 °C.[3] However, the effect of a catalyst is not so obvious, e.g. in this case one prefers large plates instead of multi fibril patches or onions. Moreover, contamination by the catalyst itself should be avoided. In this paper, we concentrate especially on the process in which carbon is turned into plate-like graphite via the intermediate phase of plate-like Al_4C_3. A crucial role in improving the graphitization plays a high-pressure-high-temperature-plasma-sintering device. We are also making use of the recently published thermodynamic data of the Al_2O_3–Al_4C_3 phase diagram.[5,6] In earlier papers we reported on graphitization of wood charcoal, liquid mixed with Al-triisopropoxide[7] and on graphitization of wood charcoal mixed with Al_2O_3 powder particles.[8] In this paper, we study the effectiveness of these two approaches, in comparison with each other.

2. Materials

Sugi (*Cryptomeria japonica*) powder was preheated in an electric furnace by increasing the temperature with 4 °C/min

---

[*] Corresponding author. Tel.: +31 50 363 4907; fax: +30 50 363 4881.
E-mail address: P.M.Bronsveld@rug.nl (P. Bronsveld).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.07.023

from room temperature to 500 °C under an argon atmosphere. Graphitization was studied in wood charcoal prepared in two different ways, one by suspension mixing with Al-triisopropoxide and one by powder mixing with 40 μm Al_2O_3 particles. For the first approach the wood charcoal powder was soaked in an isopropyl alcohol solution of Al-triisopropoxide. After soaking for 24 h, the specimen was dried at 100 °C for 24 h, put through a sieve with a 1.27 mesh size and heated by a direct pulse heating apparatus (Plasman, S S Alloy, Hiroshima). The weight percentage of aluminum oxide was 0, 10, 20 and 30% based on the weight of dry wood charcoal. The graphitizing temperature was up to 2200 °C and the reaction time was 5 min.

For the second approach the charcoal was mixed with 40 μm sized aluminum oxide powder particles and then graphitized in the direct pulse sintering apparatus. Electric pulse and pressure were directly applied to the wood charcoal powder inside the die. The weight percentage of aluminum oxide was again 0, 10, 20 and 30% based on the weight of dry wood charcoal. Also here the reaction temperature was in the range up to 2200 °C, the reaction time was 5 min and the pressure was 50 MPa.

3. Methods

In order to quantify the difference between graphitization with Al-triisopropoxide and Al_2O_3 particles one should concentrate more on bulk parameters. It is with this in mind that X-ray diffraction and XPS measurements were given a more prominent role besides the electron microscopy results that were reported already in the two earlier papers.[7,8]

X-ray data were collected both for the Al-triisopropoxide sample and the Al_2O_3 powder sample on a RINT-ultra X18 X-ray diffraction device. X-ray diffraction patterns were collected on samples with different amounts of catalyst held at different temperatures.

Similarly, XPS data were collected on an AXIS-HS (Shimadzu/KRATOS) machine using an Mg Kα (1253.6 eV) X-ray source operating at 150 W in a vacuum of $2–5 \times 10^{-8}$ mbar. High-resolution scans of the C_{1s} peak were performed with the pass energy adjusted to 40 eV. The curve fitting of the XPS spectra was carried out using a nonlinear least squares curve-fitting algorithm with a Gaussian/Lorentzian product function. The Gaussian/Lorentzian mix was taken as 0.5, except for the “graphitic” carbon peak, for which 0.84 was used with an exponential tail. The C_{1s} binding energy of the graphite peak was taken to be 284.3 eV for calibration purposes.

Composition and microstructure were examined by transmission electron microscopy (TEM) and by scanning electron microscopy (SEM) to monitor the graphitization of the biomass carbon. The specimens were examined with a JEOL 2010F 200 kV transmission electron microscope equipped with a post column energy filter (GIF 2000 Gatan Imaging Filter), in a JEOL 4000 EX/II TEM operated at 400 kV and in a FEI XL 30s SEM.

4. Results

At a temperature of 2200 °C one observes a drastic change in the displacement of the dies that press the charcoal powder together, which suggests that crystallization of biomass carbon is effectively taking place. This drastic change in parameters was confirmed by electrical conductivity and thermal diffusivity measurements as well. A big change is observed between the samples with different amounts of catalyst and the original charcoal without the catalyst. It suggests a higher degree of graphitization in the treated samples. At the same time, little change was observed in those bulk properties at 2200 °C after longer times.

Pure aluminum vapor is being released during the heat treatment. It escapes from within the dies and forms a coating on the heat shield around the furnace.

4.1. X-ray diffraction

In Fig. 1a and b X-ray diffraction patterns are reproduced for samples kept at different temperatures for a 10% aluminum oxide concentration and at different concentrations for a temperature of 2200 °C, respectively. The detection of the (0 0 0 2) graphite peak can be considered as proof that mixing of charcoal with aluminum oxide powder combined

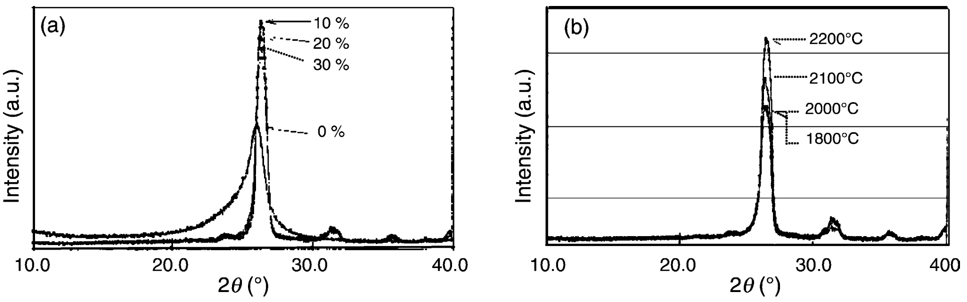

Fig. 1. X-ray diffraction patterns of samples (a) carbonized at 2200 °C with different concentration of Al_2O_3 and (b) carbonized with 10% Al_2O_3 at different temperatures.

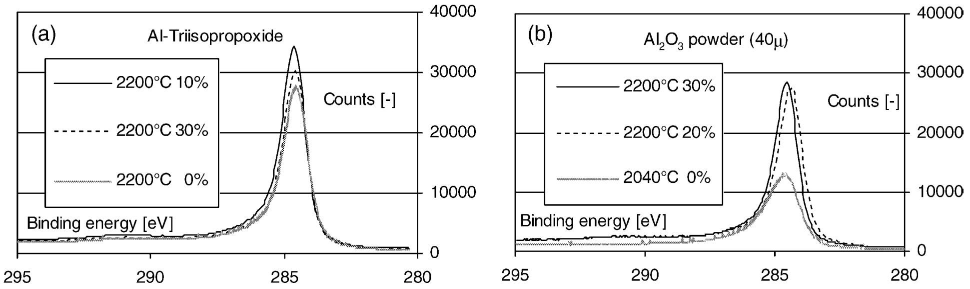

Fig. 2. XPS spectra of the C_{1s} peak for pure wood charcoal and (a) charcoal suspended in an Al-triisopropoxide solution or (b) charcoal powder mixed with Al_2O_3 (40 μm), all with the indicated wt.% and heat treatment.

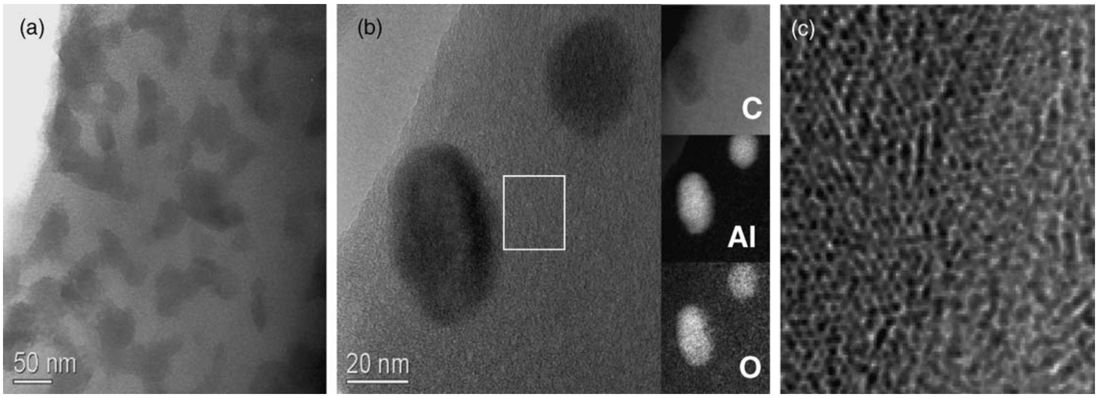

Fig. 3. Charcoal with 20% Al-triisopropoxide; 5 min at 1300 °C. (a) Overview showing dispersed catalytic particles; (b) two Al_2O_3 particles and elemental mapping by EFTEM for carbon, aluminum and oxygen; (c) detail from figure (b) (white frame).

with a heat treatment by pulse current sintering accelerates the process from carbon to graphite.

At 2200 °C, complete graphitization takes place for the Al-triisopropoxide sample as well as for the Al_2O_3 powder sample confirming the tendency in the X-rays data up to 1900 °C reported by Yu et al.[4]

4.2. X-ray photoelectron spectroscopy

In Fig. 2a and b XPS scans are reproduced for samples with from 0 to 30 wt.% catalyst heated at 2200 °C for 5 min. The samples treated with Al-triisopropoxide showed slightly higher peaks than those based on aluminum oxide particles. A nice similarity was found between the model peak C_{1s} from graphite and the peak from our sample. After applying the model of the overlapping peak of natural graphite, we added another peak, to which we set the peak position free in order to estimate the difference between the peak from the sample and that from pure graphite. After deconvolution, the area of the second peak was zero in the sample at 2200 °C treated with 20 wt.% Al_2O_3, and 27 at.% at 2200 °C without catalyst. The second peak position was covering a range from 285.3 to 288.0 eV.

Judging from these results and in combination with HRTEM images it became clear that the higher the degree of graphitization the narrower the main peak and the smaller the contribution to a second peak.

4.3. Electron microscopy

Fig. 3 is the EFTEM image of wood charcoal with 20% Al-triisopropoxide carbonized at 1300 °C for 5 min. An over-

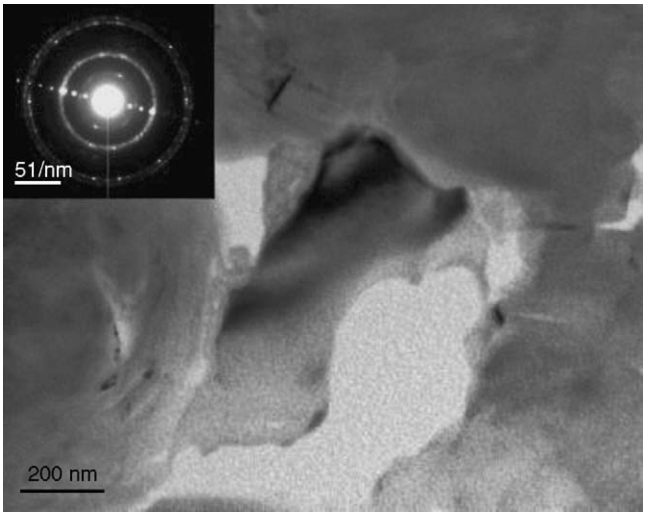

Fig. 4. An original Al_2O_3 particle turning into an Al_4C_3 plate in a sample with 30% aluminum oxide after a heat treatment of 5 min at 2200 °C. SADP of the Al_4C_3 plate with its typical 0.416 nm interplanar spacing for the (0 0 0 6) planes is enclosed.

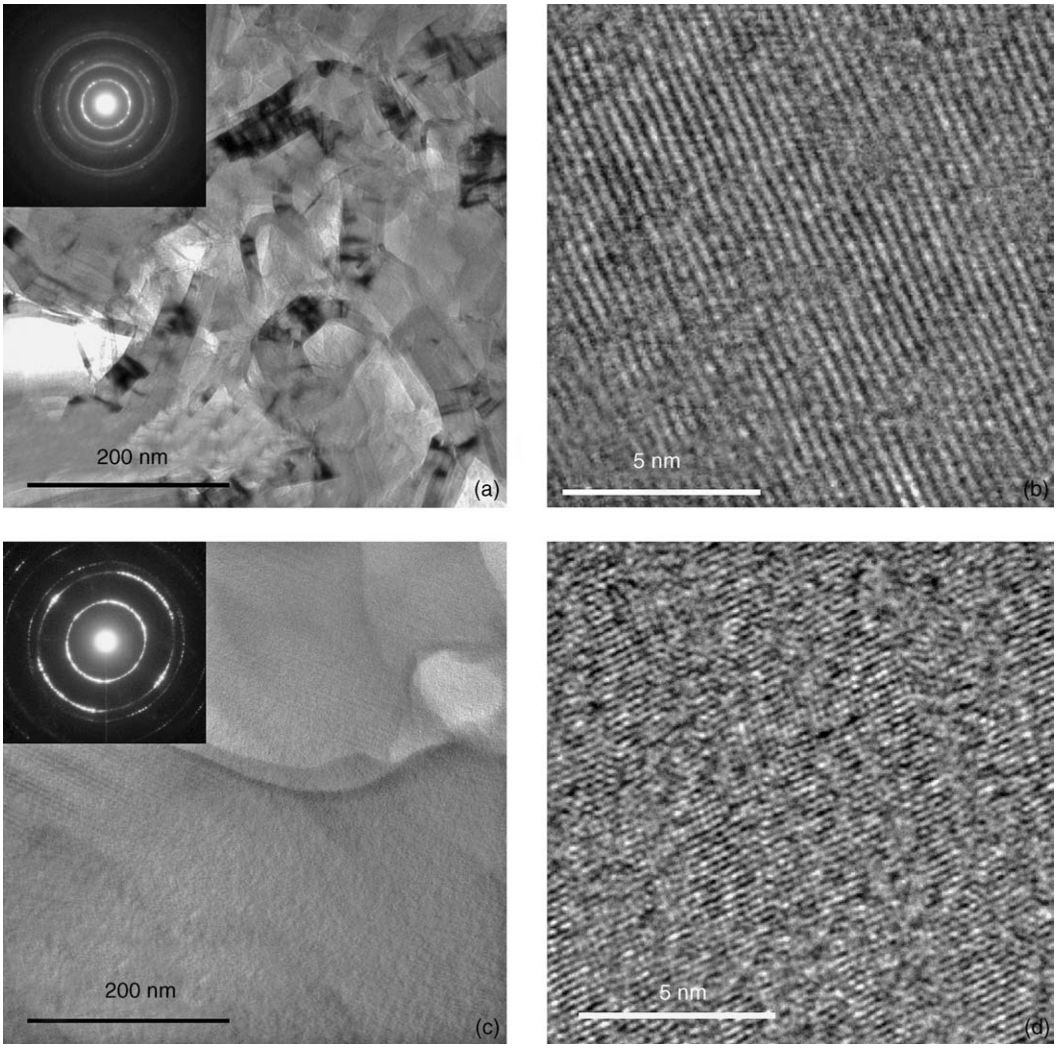

Fig. 5. Bright field TEM image of a sample with 10% Al-triisopropoxide heated at 2200 °C for 5 min; (a) BF TEM image showing fibrillar graphite, (b) HRTEM image of one of the fibrils with 0.336 nm between basal planes, (c) BF TEM image of an area where catalytic graphitization took place, (d) HRTEM image of low index planes of graphite other than basal planes due to carbide mediated graphitization.

all patchy presence of Al_2O_3 is observed. Graphitization still cannot be observed. The TEM image in Fig. 4 shows a 10 times bigger slab with its diffraction pattern as inset. It clearly shows the typical 0.416 nm interplanar spacing for the (0 0 0 6) planes in Al_4C_3 (Trigonal crystal structure, R-3m with $a = 0.333$ nm and $c = 2.499$ nm). This big slab was mapped by EFTEM and showed a decreasing amount of oxygen going from the center of the image towards the upper right hand side. Obviously, it is a particle in transition from oxide to carbide, originally occupying the central area, of which the centerpiece was removed by thinning during sample preparation. The basal planes in the Al_4C_3 plates are parallel to the long sides of the plates, indicating that the main growing direction is along the (0 0 0 1) planes. A porous reaction layer could be observed all around the Al_4C_3 plate. CO formation during the reaction between Al_2O_3 and C must be the reason for this porous structure. This was confirmed indirectly by images of Al_4C_3 plates grown in Al/SiC composites.[9] The surroundings of such plates did not show these porous reaction areas, as no oxygen was present.

In Fig. 5 the actual difference is shown between the graphitization result due to temperature alone (Fig. 5a and b) and the catalytic result (Fig. 5c and d). Two features are important to note. First of all, the homogeneous area after the catalytic transformation is at least 10 times as big as the fibril sizes. Furthermore, severe texture occurs after the catalytic process due to the plate-like growth of the Al_4C_3 along the basal planes and the subsequent transformation from carbide to graphite. The characteristic distance between the basal planes does not show up in the diffraction pattern of Fig. 5c due to an unfavorable orientation. The inner ring no longer represents (0 0 0 2) but rather the almost overlapping (10–10) and (10–11) reflections. The outer strongly textured set of rings represent (11–20) and (11–22) reflections.[10]

5. Discussions

Formation and dissociation of plate-like Al_4C_3 takes place between carbon and either Al-triisopropoxide or Al_2O_3 particles. The model phase diagram calculated by Qiu and Metselaar[6] of the pseudo-binary Al_2O_3–Al_4C_3 system is taken as starting point. It is then straightforward to choose the heat treatment in order to optimize the effect of the catalyst. The Al_2O_3 phase should give way to the Al_4C_3 phase during a heat treatment between 1990 and 2160 °C following the reaction equation

$$2Al_2O_3 + 9C\,(s) > Al_4C_3\,(s) + 6CO\,(g) \tag{1}$$

The corresponding CO pressure is 6.3 bar at 2160 °C calculated from the data in reference.[6] An experimental set-up under an argon pressure of 50 MPa with the argon flow continuously reducing the CO partial pressure to far below this value favors the formation of Al_4C_3.

The Al_4C_3 is an equilibrium phase at relatively high temperature and low CO (g) pressure and indeed Al_4C_3 plate-like crystallites were observed in the sample at 2200 °C with 30% Al_2O_3.[8]

As the Al_4C_3 phase becomes thermodynamically unstable above 2160 °C, Al (g) and C (s) occur in the Al–C–O system following the equation

$$Al_4C_3\,(s) > 4Al\,(g) + 3C\,gr\,(s) \tag{2}$$

The corresponding Al pressure is 0.3 bar at the decomposition temperature of 2160 °C based on the data in reference.[6] By lowering this partial pressure artificially by letting the Al vapour condense onto the heat shield of the furnace forces the chemical reaction of Eq. (2) towards the right hand side.

Lihrmann et al.[5] emphasise the point that the intermediate phases of Al_4O_4C and Al_2OC are being formed but not the Al_4C_3. However, we have explicit proof from SAD images[8] and backed up by the Al_2O_3–Al_4C_3 phase diagram[6] that Al_4C_3 has been formed.

6. Conclusions

The notoriously poor ability of lingo-cellulose to transform into large areas of well-ordered graphite can be surpassed by introducing the intermediate reaction between carbon and Al_2O_3 forming plate-like Al_4C_3 already coined by Sinclair the method of carbide mediated graphitization.[3] The formation energy he encountered in thin layers of a transition metal embedded by two layers of amorphous carbon was only 18 kJ/mol.[3] Both the formation and dissociation of Al_4C_3 under the proper CO pressure into Al vapor and solid graphite is confirmed by EFTEM. The wetting problem or the Al_4C_3 reaction layer forming an obstruction for further reaction between carbon and Al_2O_3 was solved, by using a pressurized, high temperature plasma sintering process and by reference to the model pseudo-binary phase diagram. The difference between Al-triisopropoxide and Al_2O_3 is a matter of intensity of the graphite reaction versus the size of the graphite patches, that means a slightly higher X-ray diffraction peak and XPS signal in the former case versus a larger plate-like structure observed with TEM in the latter case. The paper by Qiu and Metselaar[6] made the process accessible in a quantitative sense, e.g. 2160 °C as decomposition temperature of Al_4C_3, 0.3 bars as the Al vapor pressure at this temperature and 6.3 bars as the CO gas pressure.

References

1. Bundy, F. P., Pressure-temperature phase diagram of elemental carbon. *Physica*, 1989, **A156**, 169–178.
2. Oya, A. and Marsh, H., Phenomena of catalytic graphitisation. *J. Mater. Sci.*, 1982, **17**, 309–322.
3. Sinclair, R., Itoh, T. and Chin, R., In situ TEM studies of metal-carbon reactions. *Microsc. Microanal.*, 2002, **8**, 288–304.
4. Yu, J. K., Ueno, S., Li, H. X. and Hiragushi, K., Improvement of graphitization of isotropic carbon by Al_2O_3 formed from aluminum chelate compound. *J. Eur. Ceram.Soc.*, 1999, **19**, 2843–2848.
5. Lihrmann, J.-M., Tirlocq, J., Descamps, P. and Cambier, F., Thermodynamics of the Al—C—O system and properties of SiC—AlN—Al_2OC composites. *J. Eur. Ceram. Soc.*, 1999, **19**, 2781–2787.
6. Qiu, C. and Metselaar, R., Thermodynamic evaluation of the Al_2O_3—Al_4C_3 system and stability of Al-oxycarbides. *Z. Metallk.*, 1995, **86**, 198–205.
7. Hata, T., Nishimiya, K., Bronsveld, P., Vystavel, T., DeHosson, J., Kikuchi, H. *et al.*, Electron microscopic study on catalytic carbonization of biomass carbon: I. Carbonization of wood charcoal at high temperature by Al-triisopropoxide. *Mol. Cryst. Liq. Cryst.*, 2002, **386**, 33–38.
8. Hata, T., Bronsveld, P., Vystavel, T., DeHosson, J., Kikuchi, H., Ishimaru, K. *et al.*, Catalytic graphitization of wood-based carbons with alumina by pulse current heating. In Proceedings of Symposium I, E-MRS, ed. P. Scharff, 2004.
9. Ocelik, V., Vreeling, J. A. and DeHosson, J. Th. M., EBSP study of reaction zone in SiC/Al metal–matrix composite prepared by laser melt injection. *J. Mater.Sci.*, 2001, **36**, 4845–4849.
10. Hata, T., Vystavel, T., Bronsveld, P., DeHosson, J., Kikuchi, H., Nishimiya, K. and Imamura, Y., Catalytic carbonization of wood charcoal: Graphite or diamond? *Carbon*, 2004, **42**, 961–964.