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

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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\textsubscript{2}O\textsubscript{3} particles. Both types of samples were plasma sintered during 5 min under an argon pressure of 50 MPa at temperatures up to 2200 \degree C. Plate-like catalytic graphitization develops by formation and dissociation of plate-like Al\textsubscript{4}C\textsubscript{3}. Plasma sintering under the proper CO partial pressure and heat treatment temperature is instrumental in forcing the Al\textsubscript{2}O\textsubscript{3} to react with the carbon, forming first Al\textsubscript{4}C\textsubscript{3} and subsequently graphite. The difference between Al-triisopropoxide and Al\textsubscript{2}O\textsubscript{3} is a matter of intensity of the graphite reaction versus the size of the graphite patches.

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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 \degree C rather easily.\textsuperscript{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 (0002) graphite layers, a distance of 0.34 nm apart. The process of catalytic graphitization of ungraphitized carbon has been extensively studied.\textsuperscript{2,3} 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 \degree C.\textsuperscript{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\textsubscript{4}C\textsubscript{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\textsubscript{2}O\textsubscript{3}–Al\textsubscript{4}C\textsubscript{3} phase diagram.\textsuperscript{5,6} In earlier papers we reported on graphitization of wood charcoal, liquid mixed with Al-triisopropoxide\textsuperscript{7} and on graphitization of wood charcoal mixed with Al\textsubscript{2}O\textsubscript{3} powder particles.\textsuperscript{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 \degree C/min
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 Al₂O₃ 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 Al₂O₃ 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 Al₂O₃ 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 × 10⁻⁸ mbar. High-resolution scans of the C1s 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 C1s 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 200kV transmission electron microscope equipped with a post column energy filter (GIF 2000 Gatan Imaging Filter), in a JEOL 4000 EX/II TEM operated at 400kV 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 (0002) graphite peak can be considered as proof that mixing of charcoal with aluminum oxide powder combined
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 Al₂O₃ 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 C₁s 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% Al₂O₃, 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. 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 Al₂O₃ 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 (0006) planes in Al₄C₃ (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 Al₄C₃ plates are parallel to the long sides of the plates, indicating that the main growing direction is along the (0001) planes. A porous reaction layer could be observed all around the Al₄C₃ plate. CO formation during the reaction between Al₂O₃ and C must be the reason for this porous structure. This was confirmed indirectly by images of Al₄C₃ plates grown in Al/SiC composites. 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 Al₄C₃ 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 (0002) 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.
5. Discussions

Formation and dissociation of plate-like Al$_4$C$_3$ takes place between carbon and either Al-triisopropoxide or Al$_2$O$_3$ particles. The model phase diagram calculated by Qiu and Metselaar$^6$ of the pseudo-binary Al$_2$O$_3$–Al$_4$C$_3$ 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$_4$O$_3$ phase should give way to the Al$_4$C$_3$ phase during a heat treatment between 1990 and 2160 $°$C following the reaction equation

$$2\text{Al}_2\text{O}_3 + 9\text{C} (s) \rightarrow \text{Al}_4\text{C}_3 (s) + 6\text{CO} (g)$$  \hspace{1cm} (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$_4$C$_3$.

As the Al$_4$C$_3$ phase becomes thermodynamically unstable above 2160 $°$C, Al (g) and C (s) occur in the Al–C–O system following the equation

$$\text{Al}_4\text{C}_3 (s) \rightarrow 4\text{Al} (g) + 3\text{C} (s)$$  \hspace{1cm} (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.$^3$ emphasise the point that the intermediate phases of Al$_2$O$_3$C and Al$_2$OC are being formed but not the Al$_4$C$_3$. However, we have explicit proof from SAD images$^8$ and backed up by the Al$_2$O$_3$–Al$_4$C$_3$ phase diagram$^8$ that Al$_4$C$_3$ 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$_2$O$_3$ forming plate-like Al$_4$C$_3$ already coined by Sinclair the method of carbide mediated graphitization.$^5$ The formation energy he encountered in thin layers of a transition metal embedded by two layers of amorphous carbon was only 18 kJ/mol.$^7$ Both the formation and dissociation of Al$_4$C$_3$ under the proper CO pressure into Al vapor and solid graphite is confirmed by EFTEM. The wetting problem or the Al$_4$C$_3$ reaction layer forming an obstruction for further reaction between carbon and Al$_2$O$_3$ 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$_2$O$_3$ 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$_4$C$_3$, 0.3 bars as the Al vapor pressure at this temperature and 6.3 bars as the CO gas pressure.

References