

FORMATION OF SILICON CARBIDE NANOWIRES FROM ANTHRACITE SURFACES

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Introduction

A simplified process has been devised for growing Silicon carbide nanowires (SCNWs) on the surface of anthracite fines. Yet further, the SCNWs generated herein were then tested so as to discern their mechanical strength for binding the anthracite fines together at extremely high temperatures. For full-scale foundry cupola applications, there are several interesting points associated with the environment that the SCNWs were proposed to be applied in. First, high temperature conditions exist in the cupola furnace[1]; and the typical temperature above the iron melting zone is from 1000 °C to 1400 °C. So the first question was whether the SCNWs could grow well within this temperature range. Secondly, the anthracite fines contain considerable traces of metals; and the question was whether these could effectively catalyze the growth of the SCNWs. The third question was whether there would be an appropriate balance of raw materials for the SCNWs to grow without a continuous inflow of precursors.

Experimental

The anthracite fines used in this study were obtained from Jeddo Coal Company (Hazleton, Pennsylvania). Most of these anthracite grains (about 97%) used herein were within the range of U.S. mesh #10 × 80 (2000 μm to 179 μm); unless otherwise identified as powdered anthracite. The silicon metal was purchased from Alfa Aesar (Ward Mill, MA) as 98.4% silicon lumps. The lumps were crushed into silicon powder by a ball mill; and then screened to less than U.S. mesh #100 (150 μm) sieve. The typical grain size of the silicon powder used herein was 10 to 20 μm as observed by SEM.

Anthracite fines were dried at 105 °C overnight to remove their moisture content. Then 100 grams of anthracite fines were mixed with 10 grams of silicon powder (i.e. 9% Si). Meanwhile, collagen binder (1 gram by dry weight) was dissolved in 12 mL water at 70 °C to form a gelatin sol. The anthracite and silicon mixture were added into this sol with constant mixing. The final mixture was packed into a cylindrical mold (2.9 cm dia. x 4.8 cm long) with about 280 kPa pressure applied on both ends. Finally, the pellet was extruded from the mold and cured under ambient conditions. At least three anthracite pellets were produced for each recipe and protocol, so as to achieve statistical replication.

The pyrolysis of the anthracite pellets was conducted in a horizontal alumina tube furnace. A slow nitrogen gas flow (~2 standard cubic centimeters per minute) was used to prevent the anthracite from burning. A three-step pyrolysis procedure was employed. First the furnace was ramped up at 3 °C/min to the 1400 °C. Then this temperature was maintained for 2

hours. Finally the furnace was cooled down to room temperature at 3 °C/min again.

SEM and EDS were performed on samples (both before and after thermal treatment) via an FEI Quanta 200 Environmental SEM. The instrument was operated under low-vacuum conditions (10-103 Pa) using a Gaseous SE detector. The high voltage was set at 20 kV and the spot size of the electron beam was set at 4 nm. The EDS spectrums were collected from 0-10 keV within 60-seconds. A transmission electron microscope (TEM, Model 2010, JEOL, Tokyo, Japan) was used for electron diffraction; and to determine the morphology and particle size.

Real-time high-temperature XRD tests were also performed on the PANalytical X'Pert Pro MPD diffractometer. The anthracite pellets were pulverized before the pyrolysis. Next, the powders that contained both silicon and anthracite were placed on an alumina strip. A vacuum condition was provided around the alumina and the strip was heated from room temperature to 1400 °C at 100 °C per minute. Once the temperature reached 1400 °C, the diffractometer started to collect diffraction signals from 10° to 70° repeatedly. Each scan from 10° to 70° took about 7 minutes, so the real time change of the XRD pattern at 1400 °C could be observed in this way.

Result and discussion

The SEM images of these treated anthracite fines in Figure 1 exhibited nanowires that grew from the surface of the anthracite. Intensive silicon carbide nanowires were formed from the surface of the anthracite fines, and they almost covered the anthracite fines entirely. The high resolution SEM images in Figure 1b&c show that the SCNWs grew into a massive network. It seemed that many nanowires connected with each other. These junctions of nanowires could be confirmed from the TEM image in Figure 2. The EDS response from the nanowires Figure 1d indicated that carbon and silicon were the major elements in the nanowires. Trace amounts of oxygen and aluminum were also frequently detected by the EDS. Aluminum was particularly prominent in ashed samples of anthracite fines. This native aluminum could have served as a catalyst for nanowire growth.

The TEM images of the nanowires (Figure 2) confirmed that the diameters of the nanowires ranged from 30 to 60 nm. One unique feature of the SCNWs growth found in this study is that some of the SCNWs joined to one another at junctions. Some SCNWs jointed almost perpendicular into other SCNWs, and one of the wires often stopped growing as it teed into another. From the structural view point, these junctions were perceived as desirable in the anthracite binding application as they provided extra strength for the system. In the TEM image in Figure 2, there were about half as many junctions as there were SCNW. Our Carbon conference presentation will exhibit yet further TEM images with similar proportions of junctions. This finding was also not contradicted by the highest resolution of SEMs in Figure 1.

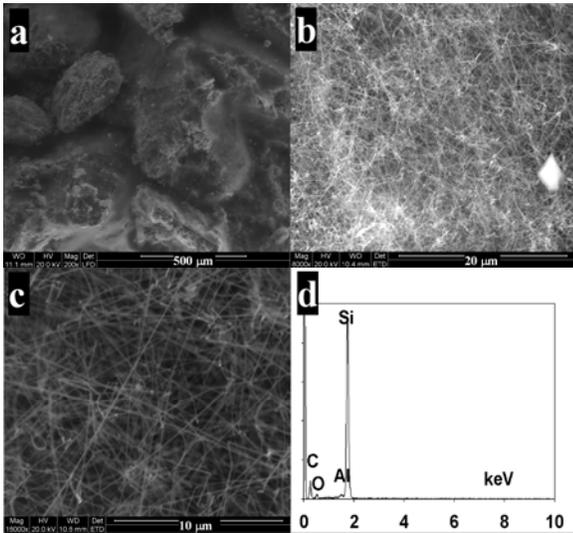


Fig. 1 SEM images of silicon carbide nanowires grown from anthracite fines (d) is the EDS spectrum of the nanowires.

Also in the lower-right corner of Figure 2, the selected area electron diffraction (SAED) pattern of a SCNW exhibited a perfect hexagonal reciprocal lattice of the (111) in the 3C-SiC crystal structure. The trace of stacking of the 3C-SiC (111) lattice planes along the [111] direction could be identified from some portions of the SCNWs in Figure 2. This [111] growth has also been shown by others [2, 3]. In the lower left corner of Figure 2, twin growth of two SCNWs was also observed, which normally shows a 70.5° between the growth direction and the (111) plane [3, 4]. One interesting feature in Figure 2 is that the two nanowires twinning from the substrate were probably separated by the incoming of a third nanowire. At least one of the twinning nanowires continued growing and changed its direction to the typical stacking along [111].

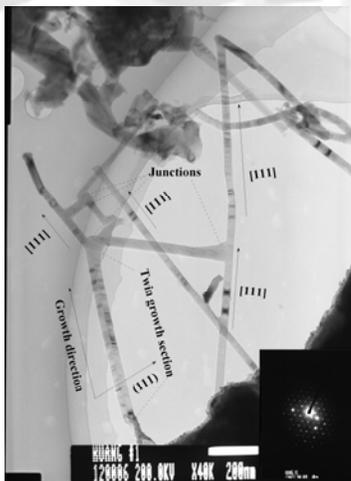


Fig. 2 TEM image of the SCNWs grown from anthracite fines. The lower-right corner insertion is the selected area electron diffraction pattern of the SCNWs

This formation of silicon carbide at 1400 °C was very fast as shown by the real-time XRD patterns in Figure 2. When the temperature reached 1400 °C, the elemental silicon had already disappeared from the XRD pattern, probably due to

the vaporization of the silicon. Diffraction peaks from the (111) lattice plane of 3C-SiC appeared in the second scan at 1400 °C. The intensity of this response did not significantly increase with yet further time than 14 minutes. Indeed, even after 2 hours at 1400 °C, this SiC intensity had not increased.

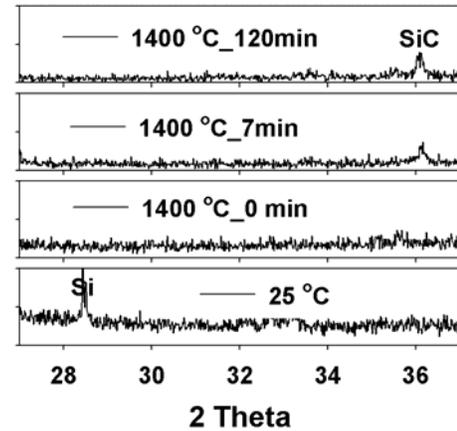


Fig. 3 Real-time change of the XRD pattern at 1400 °C within mixed anthracite and silicon powders

After the thermal treatment, the bindered anthracite fine pellets exhibited an unconfined compressive strength of 690 kPa (100 psi). When the pellets used anthracite powder (<150μm), the unconfined compressive strength of the pellets that had experienced 1400°C pyrolysis was 3.6MPa (500 psi).

Conclusion

SiC nanowires could be grown through a simple protocol that employed relatively inexpensive solid precursors. Metal impurities in the anthracite fines apparently served as the catalyst for the SCNWs to grow via a VLS mechanism. The SCNWs produced in this study have the typical cubic zinc-blende crystal structure. These nanowires provided strong binding strength to hold the anthracite fines together even after exposure to extremely high temperature. Results in this study showed a promising application of SCNWs in binding carbon materials.

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References

- [1] Huang H, Wang YJ, Cannon FS. Pore structure development of in-situ pyrolyzed coals for pollution prevention in iron foundries. *Fuel Process Technol.* 2009;90(9):1183-91.
- [2] Dai HJ, Wong EW, Lu YZ, Fan SS, Lieber CM. Synthesis And Characterization Of Carbide Nanorods. *Nature.* 1995;375(6534):769-72.
- [3] McMahon G, Carpenter GJC, Malis TF. On The Growth-Mechanism Of Silicon-Carbide Whiskers. *J Mater Sci.* 1991;26(20):5655-63.
- [4] Wang DH, Wang DQ, Hao YJ, Jin GQ, Guo XY, Tu KN. Periodically twinned SiC nanowires. *Nanotechnology.* 2008;19(21).