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Research Letter

Carbon Tubular Morphologies in Blast Furnace Coke

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The paper reports on the first occurrence of microscale carbon tubular morphologies (CMTs) in a blast furnace (BF) coke. The CMTs were probably formed as a result of the conversion of solid disordered carbon via liquid phase metal particles involving a gas phase containing a substantial amount of N_2 and O_2. The presence of CMTs may lie behind the generation of the smallest fraction of fines in BF exhaust dust. If the amount of CMTs present in the BF exhausts gases at any particular metallurgical site proves to be substantial, it could become a subject of environmental concern.

1. INTRODUCTION

Carbon tubular morphologies are mostly known as nanotubes and microtubes, implying internal diameters in the nanometer or micron range, respectively. Carbon nanotubes, which can be single (SWNT) or multiwalled (MWNT), have many properties that make them potentially useful in a wide variety of applications, including composites, electronics, pharmaceuticals, and optics. They are also known for the environmental and health risks attached to them [1–6]. SWNTs can be synthesized by arc discharge, laser oven, and chemical vapor deposition techniques, and one feature common to all these procedures is that metal catalysts play an important role in their growth [7]. The most popular model for SWNT formation is "the vapor-liquid-solid model, in which carbon from the vapor phase is deposited onto liquid-phase metal carbide particles, from which the nanotubes then grow" [8]. There is also a solid-liquid-solid (SLS) model, which suggests the conversion of solid disordered carbon into nanotubes via liquid phase metal particles [9]. As for MWNTs, arc evaporation produces the best-quality tubes, by three types of mechanism, referred to as "gas," "solid," and "liquid" phase models [8]. "The gas phase models assume that nanotube nucleation and growth occur as a result of direct condensation from the vapor, or plasma, phase. In solid phase models, the nanotubes and nanoparticles do not grow in the arc plasma, but rather form on the cathode as a result of a solid state transformation. A variant of the solid state model envisages a "crystallization" of nanotubes from extended assemblies of disordered carbon, while the liquid phase model assumes that nanotubes nucleate within globules of liquid carbon deposited onto the cathode" [8]. It was also found that heat treatments could produce micron-length SWCNTs at about 1000–1300°C [8].

The features and mechanisms of formation of carbon microtubes (CMTs) are characterized in literature to a lesser extent than those of SWNTs and MWNTs. They are known as "ideal candidates for microfluidic applications such as micropumps, flow channels and nano-/microreactors" [10]. CMTs with controlled conical angles can be synthesized in a microwave plasma CVD chamber at 600–1100 W and a reactor pressure of 40–90 Torr, for example, by spreading of a thin film of gallium onto a graphite substrate followed by dusting with molybdenum powder using different N_2/O_2 dosages [10]. This paper represents the first description of microscale carbon tubular morphologies found in samples of blast furnace coke and discusses possible mechanisms for their formation.

2. SAMPLES AND METHODS

Metallurgical coke, a key material for BF operation, is made from mix of several coals by heating it to 1100–1200°C in coke ovens consisting of two walls spaced about 40–45 cm apart. The coke is charged into the BF along with the iron

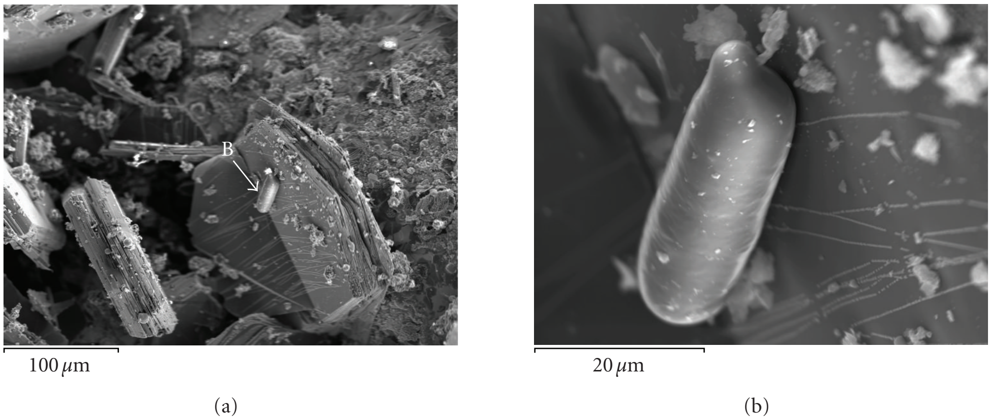


FIGURE 1: The SEM image of CMT attached by its long axe to (0001) face of a flake-like graphite crystal, sample 30424109-35.

ores, various fluxes, and scrap and takes part in solid-to-solid, solid-to-melt, and solid-to-gas reactions that occur inside the BF. The coke located in a BF is referred to as BF coke. The temperature at a tuyere level, where hot air is blown into the BF, exceeds 2000°C.

A number of samples of BF coke from two drill cores (30424109 and 130303203) were studied. The samples were obtained from the tuyere zone of an operating BF at Ruukki Steel Works in Raahe, Finland, using a mobile tuyere rig [11]. They were cut under dry conditions (no cooling water used in sawing), preserving one original surface, and sections about 35–40 mm long, 20–25 mm wide, and c. 5–7 mm thick were then fixed to glass plates. These dry-cut sections were studied with a stereomicroscope and then with a Jeol JSM-6400 scanning electron microscope (SEM) equipped with an energy-dispersive spectrometer (EDS). Two of the samples which contained CMT-like (CMT thereafter) carbon tubular morphologies are described here, the first selected from a point 35 cm from the tuyere level (drill core 30424109), and the other from 70 cm away (drill core 130303203).

3. RESULTS AND DISCUSSION

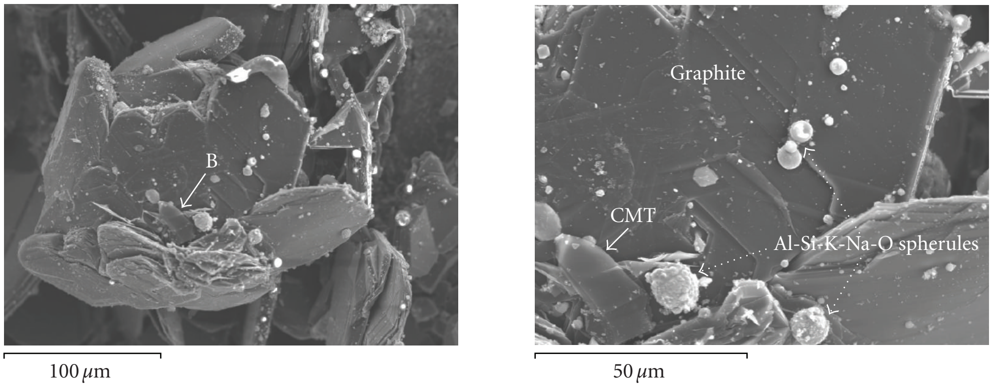
Three CMTs were found in two samples, two in sample 30424109-35 and one in sample 130303203-70. Stereo microscopy revealed that the sample surfaces hosted a number of droplets of molten iron of diameter from 0.1 to 5 mm, some of the droplets being surrounded by a 0.5–1.5 mm zone of graphite crystals. SEM/EDS studies indicated that the iron droplets were covered by a thin carbon shell that caused a dull metallic luster in a stereomicroscopic view.

The first CMT, in sample 30424109-35, was attached by its long axis to the (0001) face of a flake-like graphite crystal (see Figure 1) in which stacks of graphitic micro- and nanosheets were rotated along [0001]. The tube was c. 40 μm in length and about 13-14 μm in diameter, but with the diameter decreasing asymmetrically to end in a cone. The angle between the end of the tube and its axis was about 26–30°. The formation of a conical angle may reflect local fluctuations in the N_2/O_2 ratio in the air blown into the tuyere zone of the BF, since variations in nitrogen and oxygen dosing are known to have an effect on the conical angles of CMTs during their growth [10].

The second CMT-like particle was again observed in sample 30424109-35, where it was also attached to the 0001 face of a flake-like graphite crystal (see Figure 2) representing part of a complex aggregate of such crystals. This tube was about 30 μm in length and 10 μm in diameter and had a “cut” cone on its top and a cylindrical base. The middle part of the tube and the cone at its “bottom” had different orientations of their axes, probably also a result of changes in the N_2/O_2 ratio during particle growth. The particle was spatially associated with aluminosilicate spherules attached to the (0001) face of the graphitic host.

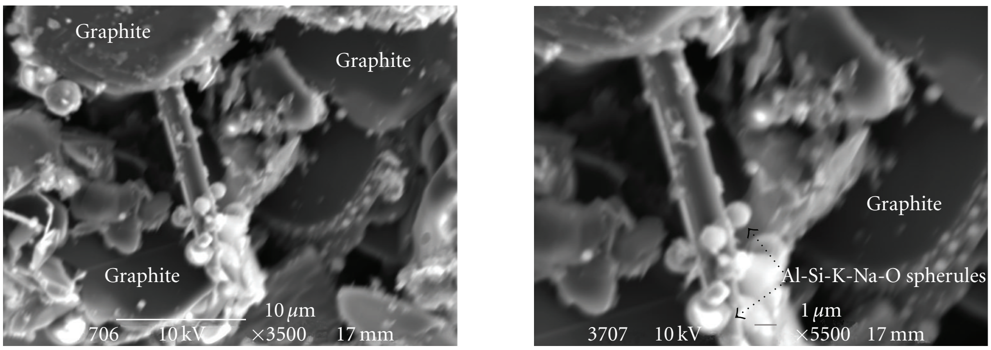
The third CMT was identified in sample 130303203-70, where it was located between two graphite flakes with an undeveloped hexagonal prism and had several aluminosilicate spherules attached to its surface (see Figure 3). The “low” end of the tube was conical in shape, but the other was obscured by the graphite crystal. The diameter of the middle part of the tube was about 2 μm and the length of the (visible part of the) tube was about 12–14 μm.

The relationships between the CMTs and the graphite crystals in the samples suggest that the CMTs are “younger” (formed later) than their graphitic hosts. The close association of the CMTs with the graphite crystals appears to be not only spatial but also genetic in character and may be related to the catalytic effect of molten iron or some other metal present in the primary coke and inherited from the coking coals. Details of the appearance of the graphite and a model for its formation in the BF coke have been discussed recently [12], together with data on earlier experimental studies [13]. The formation of graphite in BF coke seems to be a result of iron melt penetration through an unordered carbon matrix, initiating dissolution-precipitation sequences which leave the well-ordered graphitic carbons behind. The temperature estimates for this process were all around 1500°C [13], well below graphitization temperatures, due to the catalytic effect of molten iron. The present data are insufficient to allow an unequivocal explanation to be given for the origin of the CMTs in these samples. Taking into account the data on graphite growth in BF coke [12, 13], it would be reasonable



(a) (b)

Figure 2: The SEM image of CMT-like particle with a "cut" cone on its top and a cylindrical base, sample 30424109-35.



(a) (b)

Figure 3: The SEM image of CMT located between the two graphite flakes, sample 130303203-70.

to suggest that the conditions of CMTs formation were comparable to those reported by Gorbunov et al. [9] for the conversion of carbon into SWCNTs via liquid phase metal particles (the solid-liquid-solid model discussed above). The authors of the model suggested that "the first stage involves a molten catalyst nanoparticle penetrating a disordered carbon aggregate, dissolving it and precipitating carbon atoms at the opposite surface. These atoms then form a graphene sheet, whose orientation parallel to the supersaturated metal-carbon melt is not energetically favorable. Any local defect of this graphene sheet will, therefore, results in its buckling and the formation of a SWCNT nucleus" [9]. Thus, the "graphitic" model [13] and the model for CMT formation [9] have a number of features in common, and it seems that graphite crystals and CMTs are products of different parts of (or stages in) one metal-catalyzed process. Among the metals, which are known for their catalytic effect for nanotube formation, are, for example, Fe, Ni, and Co [8, 9]. As we have reported earlier, these metals are common constituents of the BF coke together with Al, Mg, Ca, Zn, and Mn [14]. Many other metals, including Co and Sn, could affect this process in the BF since these elements present in complex iron ores and scrap used for ironmaking.

The formation of CMTs may lie behind the generation of the smallest fraction of fines in the BF exhaust dust, in the same way as we suggested earlier for the tiny graphite crystals formed in BF coke [12]. This is because CMTs can easily be captured by the circulating BF gas flows, thus contributing to the total amount of BF-generated dust. If the amount of CMTs in the BF exhaust gases proves to be substantial, it could be a subject of environmental concern, since the BF process in general is a large-scale process and this is still one of the most common methods of iron production in the world and one of the major industrial polluters. Similar reasoning can be applied to the combustion of other types of coke (pitch coke, petroleum coke). Successful examples of dust management in pyrometallurgical processes by mechanical and magnetic separation have been published earlier [15], but it has not been reported so far whether CMTs can be captured in this way. In the case of the Ruukki Steel Works at Raahe, Finland, the average annual amount of all inhalable particles (under 10 μm) in the air as monitored at three stations near the factory and in the city of Raahe was in the range 16.1–19 micrograms/m^3 in 2006 [16]. This is well below the average annual limit of 40 micrograms/m^3 [16], and of course CMTs must account for only a fraction of this amount. Nevertheless, further research is needed to clarify this issue with respect to more representative set of samples of BF cokes from different sites, since the ability to produce CMTs can depend on the reactivity and composition of a particular coke in the BF process and the process conditions themselves.

4. CONCLUDING REMARKS

(i) CMT-like carbon tubular morphologies can be formed in a BF coke. (ii) They are associated with graphite crystals and are formed later than their graphitic hosts. (iii) The appearance of CMTs and associated graphite seems to be the result of a metal-catalyzed process involving a gas phase containing a substantial amount of N_2 and O_2. (iv) The presence of CMTs may lie behind the generation of the smallest fraction of fines in BF exhaust dust. If the amount of CMTs present in the BF exhaust gases at any particular metallurgical site proves to be substantial, it could become a subject of environmental concern. Modern iron production facilities can control this form of pollution, for example, by installing monitoring stations to measure the amounts of inhalable particles (under 10 μm) in the air.

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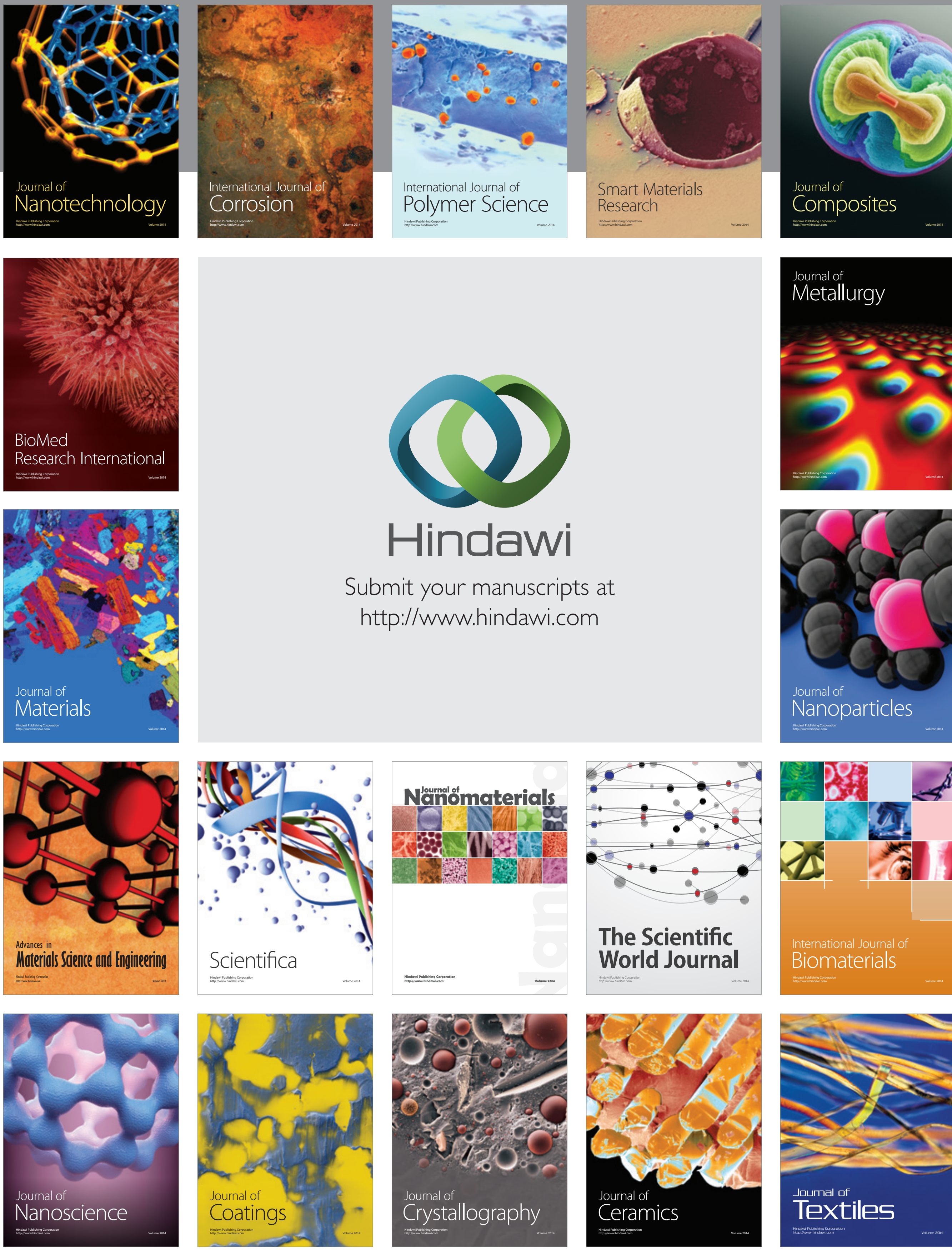
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