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Solid-phase production of carbon nanotubes

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Abstract. Graphite fragments are generated when metal carbide powders (e.g., Al_4C_3) are heated to 1000–1100 °C for 2–4 hr in an argon flow. Carbon nanotubes are formed when metal powders, e.g. Fe, Co, Y and Ni, are also present.

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In the manufacture of cast iron, small amounts of carbon (e.g. 2–4% by weight), as well as trace quantities of other elements (e.g. S, Mn, P) are routinely added to the molten metal in order to enhance specific properties of the product [1, 2]. The resulting materials have been well studied and various types of graphitic structure are known to permeate the metal [3, 4]. Recently, a possible model was proposed to account for the generation of spheroidal graphite particles in cast iron (so-called SG iron) [5], involving the coalescence of graphite slivers to form onion-structured spheroidal nuclei which then grow by accretion. It is feasible that additives, such as Ce or Mg, may act as preliminary nucleation sites, so promoting cage graphite aggregation. Thus reorganization and self-assembly of carbon during metal solidification is well-recognized, although many fundamental aspects of the precise growth mechanisms involved remain to be elucidated.

In addition to graphite, carbide phases such as Fe_3C appeared to be well-characterized constituents of cast iron. Depending on the cooling rate (or duration of the annealing process), carbon released from the homogeneous carbide phase migrates to heterogeneous localized bulk graphite sites or to other forms of aggregated carbon particles [3–5].

In an attempt to shed further light on the behaviour of carbon during the metal solidification process, we recently initiated a study of the thermal segregation of graphite from metal carbides[1]. Unexpectedly, we have found that carbon nanotubes are also generated when other metals (e.g. Fe, Co, Ni and Y) are present, but not in their absence. This discovery is a useful and intriguing new addition to the methods available for the *condensed*-phase production of carbon nanotubes, as typified by the electrolysis of carbon in molten ionic salts [6–8]. Other methods, e.g. arc discharge of graphite [9–11], pyrolysis of hydrocarbons [12, 13] and laser ablation of graphite [14, 15], appear to involve a gas–solid reaction.

The results are listed in Table 1. Upon heating to 1000–1100 °C, two carbides (MoC and Cr_3C_2) do not change color, whereas some of the other metal carbides examined (e.g. Al_4C_3, CaC_2, WC, TiC and TaC) darken. X-ray powder diffraction measurements revealed the presence of the distinctive 001 graphite reflection centered at $2\theta \cong 26°$ corresponding to separation of the graphite basal planes. This indicates that graphite has formed in the case of CaC_2, TaC and Al_4C_3, but not in the case of WC, TiC, MoC and Cr_3C_2. Al_4C_3 in particular showed a trace of the hk0 graphite reflection which indicates that larger domains of graphite are forming (ca. 20–100 nm in-plane diameter) then is the case with other carbides.

Individual graphite fragments were clearly observed (TEM, 20–100 K magnification) when Al_4C_3 was heated. HRTEM measurements (e.g. 400–600 K magnification) on other carbides (e.g. TaC and CaC_2) revealed the presence of smaller graphite domains (ca. 2–10 nm thick) with well-

Table 1. X-ray diffraction and TEM measurements of heat-treated metal carbides. ○ means yes; × means no

Metal carbides	original color changed into black after heating	X-ray diffraction showed 001 graphite reflection	X-ray diffraction showed hk0 graphite reflection	observable graphite fragments by TEM (20–100 K magnification)
CaC_2	○	○	×	×
MoC	×	×	×	×
TiC	○	×	×	×
Cr_3C_2	×	×	×	×
Al_4C_3	○	○	○	○
TaC	○	○	×	×
WC	○	×	×	×

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[1] Metal carbide powders (325 mesh) were obtained from Aldrich Ltd, UK. In a typical experiment, a quartz boat (3 cm in length) was filled with a metal carbide (200 mg), the boat was inserted into a silica tube (6 mm inner, 8 mm outer diameter), which was placed in an electric oven. An argon flow (99.99%, pureshield argon, BOC Gases) was passed through the tube at ca. 0.6–1 cm^3/s and the oven temperature was raised (30 °C/min) to 1000–1100 °C. This temperature was maintained for 4 hr (duration of each experiment). Heating was then discontinued and the sample was allowed to attain room temperature while the argon flow was maintained.