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GROWTH OF FILAMENTARY CARBON ON METALLIC SURFACES DURING THE PYROLYSIS OF METHANE AND ACETONE

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Abstract—Transmission electron microscopic studies have been carried out on iron, nickel and stainless steel surfaces, which have been subjected to gases known to produce deposition of carbon during gas phase pyrolysis. The formation of filamentary carbonaceous deposits from pyrolysis of methane is dependent on the purity of the gas. A typical contaminant, such as acetone vapour, can give rise to filamentary deposits at temperatures as low as 500°C. The nature of the deposition mechanism is discussed.

1. INTRODUCTION

The catalytic formation of carbon on metallic surfaces during thermal decomposition of a variety of hydrocarbon gases has obvious industrial relevance in such processes as the poisoning of heterogeneous catalysts and the reduced efficiency of thermal transfer between metallic heat exchangers and circulating cooling gases. In the gas-cooled, high temperature nuclear reactor, small amounts of these gases may decompose catalytically in the cooler (approx 500°C) heat exchanger region with resultant corrosion of the heat exchanger walls [1]. The deposition phenomenon has associated with it a vast literature [2–4] wherein it is shown that the most active catalysts are the ferromagnetic metals such as iron and nickel and alloys such as stainless steel. The precise catalytic mechanism, however, is not known although many suggestions have been proffered. In all probability the final products result from a sequence of intermediate reactions.

It is pertinent to select a few previous studies because of their particular relevance to the following discussion. Karu and Beer [5] noted that graphitic films were obtained when nickel was employed as a catalyst for methane decomposition. Further they found that no deposit was formed at temperatures below 700°C. They suggested that the mechanism for decomposition involved catalysis by the nickel surface which also acted as a substrate for epitaxial growth of graphite.

Robertson [4, 6] observed the formation of 'flake' carbon and fibrous material, containing electron-dense 'kernels' during methane decomposition over iron, cobalt and nickel at temperatures between 650°C and 750°C. Further work by Robertson [6] comments on the possibility that the carbon deposit could arise from breakdown of traces impurities in the methane employed in his investigation.

We here present the results of transmission electron microscopic studies of typical metals and a stainless steel alloy surface which have been subjected to gases known to produce deposition of carbon during pyrolysis.

2. EXPERIMENTAL

The metallic samples employed in the study were degreased electron microscope specimen grids of nickel, iron, and 18/8 stainless steel. Such grids are convenient for a transmission electron microscopic study of filamentary growth since the filaments grow in such a way as to protrude away from the grid bars.

The pyrolysing gases employed included three samples of methane: –

(a) commercial grade methane (Matheson Gas Co.) and

(b) two samples of ultra pure methane (British Oxygen Co., Grade X and Air Products, research grade (99·99% pure)).

High purity acetone vapour was obtained by evaporation of liquid acetone which had been thoroughly degassed in high vacuum.

High purity argon and nitrogen (British Oxygen Co., Grade X) were employed to establish that heating to high temperature in 'inert' gases did not produce any observable deposits.

The pyrolysis apparatus consisted of a double walled quartz reaction vessel evacuable to pressures of the order of 10^{-7} Torr, and heated to 1000°C by a high temperature muffle furnace.

Transmission electron microscopy was carried out using a Philips EM 300.

3. RESULTS

No differences were detected in the nature of the deposits from a particular gas at a fixed temperature when a metal was subjected to various gas pressures ranging from 20 to 200 Torr and to various exposure times from 15 min to 5 hr. For this reason all the results that are reported here have been selected from experiments carried out with gas at a pressure of 100 Torr and heated for 2 hr at the quoted temperature.

3.1. *Methane pyrolysis*

3.1.1 *On stainless steel.* Preliminary experiments with stainless steel heated in the 'commercial' grade methane, produced hollow filamentary growths, graphitic in nature and bearing an electron dense tip, at temperatures as low as 550°C (Fig. 1). In view of Robertson's comment[6] that trace impurities in the gas could account for the formation of deposits, two samples of ultra pure methane were subsequently employed. Under these circumstances no discernable filamentary growth was forthcoming until the stainless steel was heated to a temperature of 900°C and in excess. Such results would appear to confirm Robertson's observation about impurities, but we were not able to unequivocally characterize these impurities by mass spectroscopic analysis. Figure 2a shows typical hollow filaments formed when stainless steel is heated at 900°C in ultra pure methane. A high resolution micrograph (Fig. 2b) shows the electron-dense tip of such filaments.

In addition to the formation of filamentary growths, it is found that whenever a grid has fractured during manipulation (after treatment under these conditions all the grids are rather brittle), a thin film of material protrudes over the massive edge of the stainless steel grid (Fig. 3a). Selected area diffraction indicates that the film has graphitic character. A high resolution study of the film (Fig. 3b) reveals the presence of numerous electron dense particles in an interwoven matrix of filaments with the interfilamentary regions filled with deposited material thus forming a fairly uniform thin film of carbon.

3.1.2 *On nickel and iron.* No filamentary growths were observed on either nickel or iron when heated in ultra pure methane at temperatures below 900°C. At 900°C both iron and nickel were found to be more efficient catalysts than stainless steel for filamentary growth, nickel being more effective than iron.

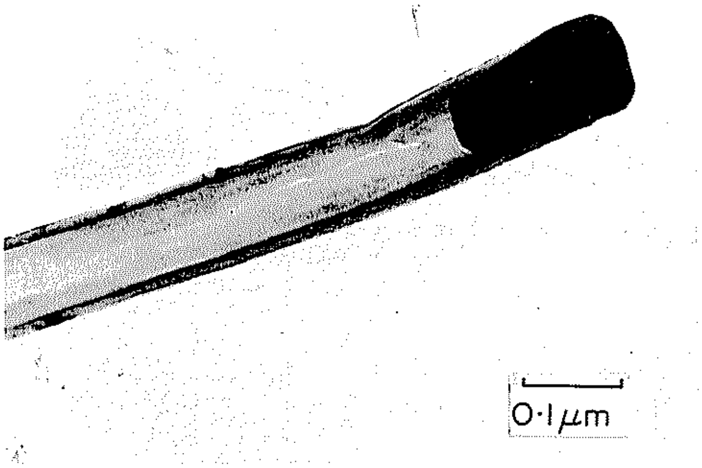

Fig. 1. Hollow filamentary growth, graphitic in nature, bearing an electron dense tip formed on exposure of stainless steel to commercial grade methane at 550°C.

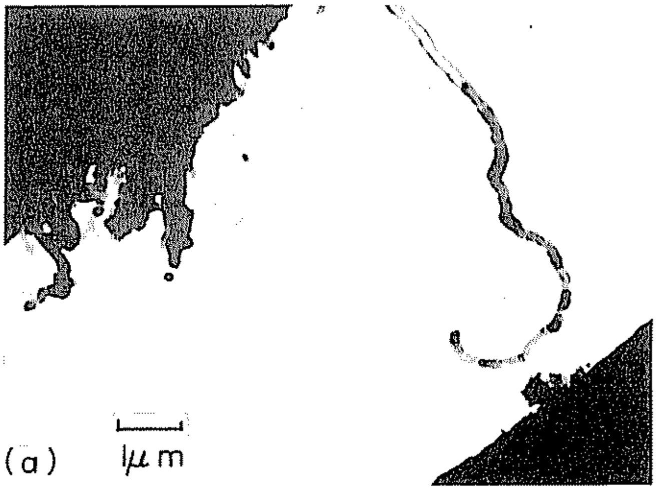

Fig. 2a. Typical filaments formed when stainless steel is heated at 900°C in ultra pure methane.

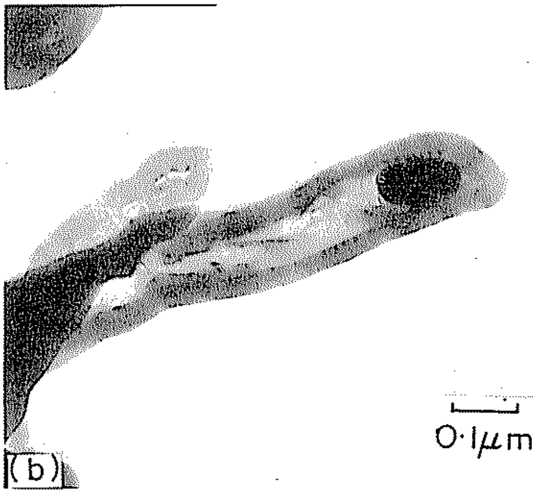

Fig. 2b. High resolution micrograph of filaments formed when stainless steel is heated at 900°C in ultra pure methane. Note electron dense tip.

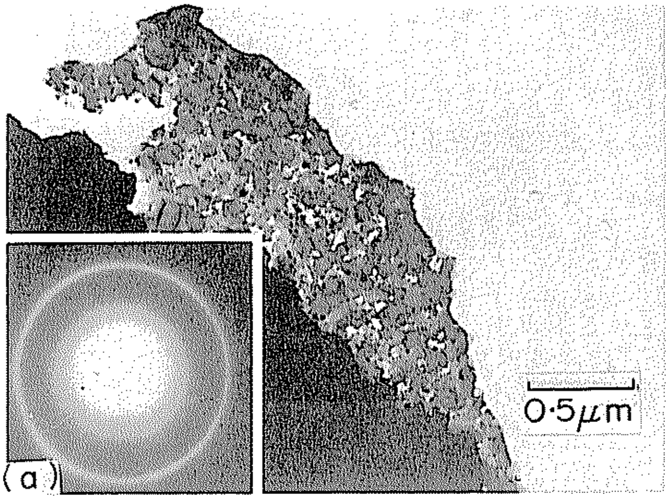

Fig. 3a. Thin film of polycrystalline graphite protruding over the fractured edge of a stainless steel grid heated in methane at 900°C. (Inset) Selected area diffraction pattern of corresponding area.

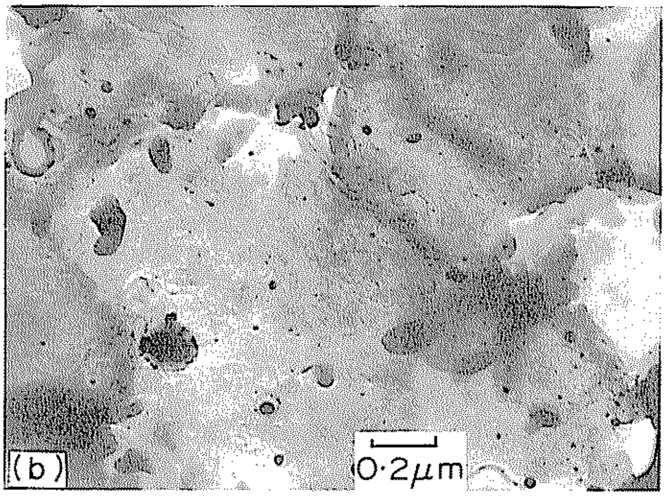

Fig. 3b. High resolution micrograph of sample shown in Fig. 3a revealing numerous electron dense particles in the thin film.

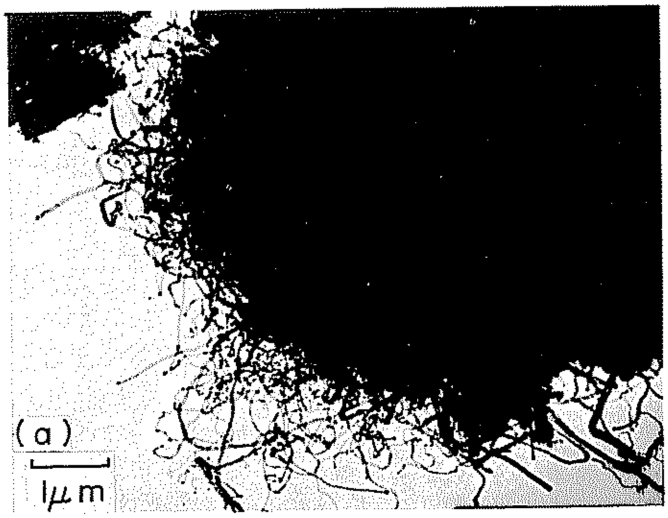

Fig. 4a. Prolific formation of filaments when nickel is heated in methane at 900°C.

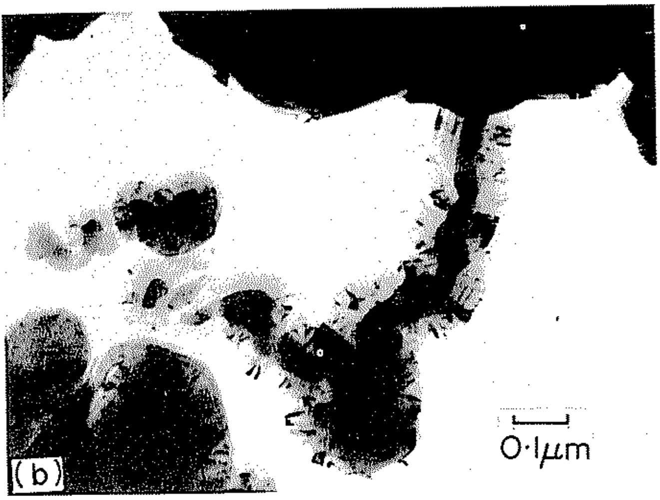

Fig. 4b. High resolution micrograph of filament formed when nickel is heated in methane at 900°C. Note numerous elongated electrondense particles along the core.

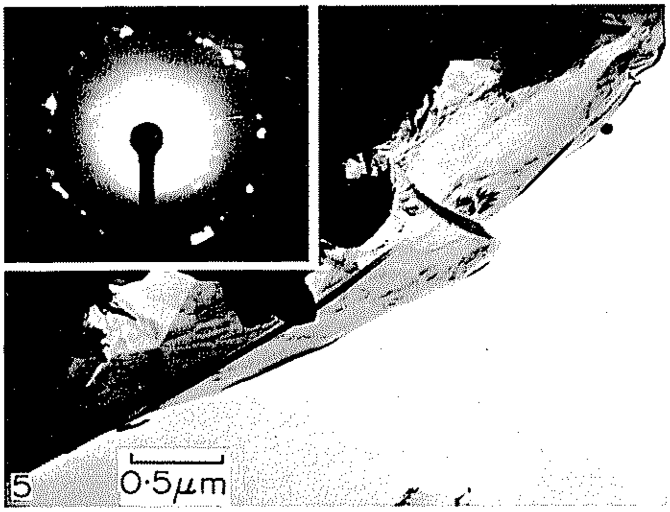

Fig. 5. Crystalline graphite formed on nickel when heated at 900°C in methane. (Inset) Corresponding selected area diffraction pattern.

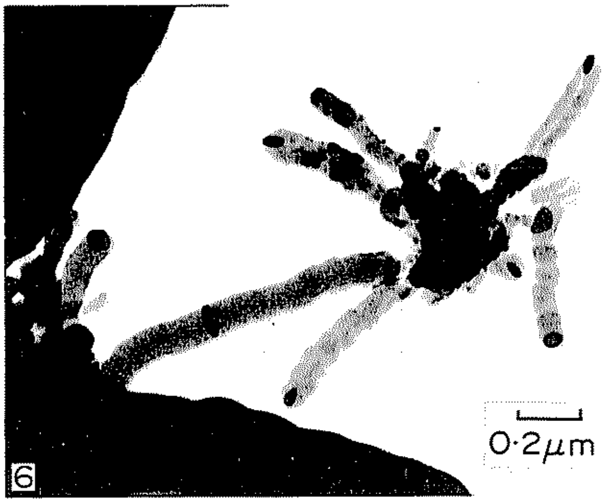

Fig. 6. Numerous filaments emanating from a central stem formed when iron is heated in methane at 900°C.

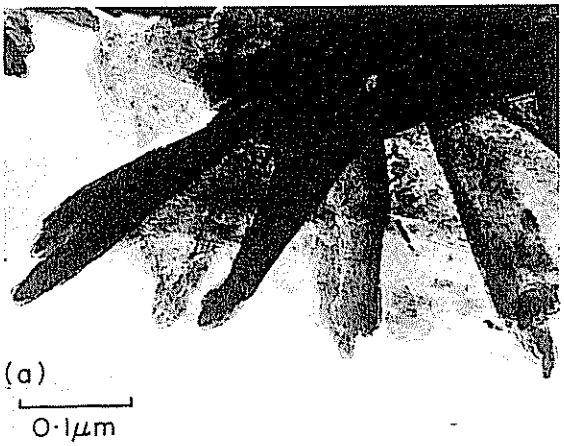

Fig. 7a. Formation of γFe_2O_3 on iron heated at 400°C in acetone.

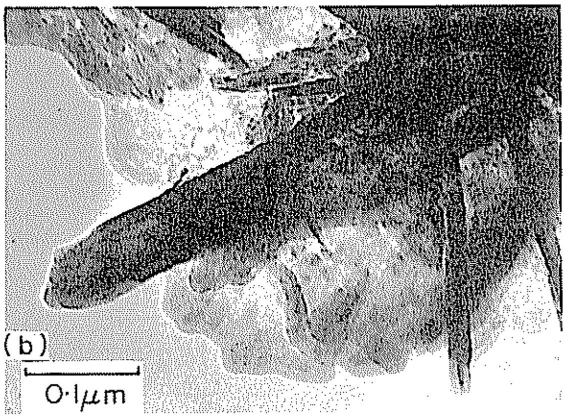

Fig. 7b. Same area as Fig. 7a rotated through 25°.

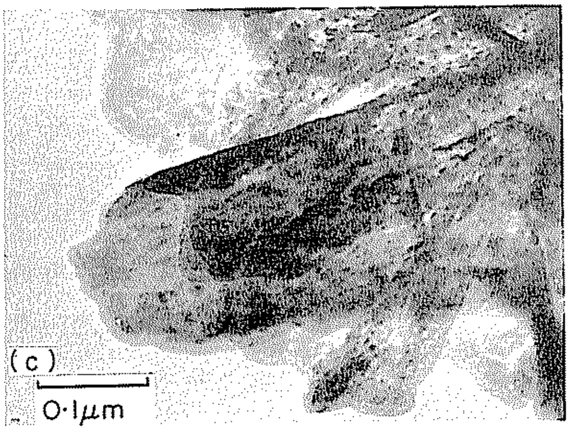

Fig. 7c. Same area as Fig. 7a rotated through 50° showing acicular nature of deposit.

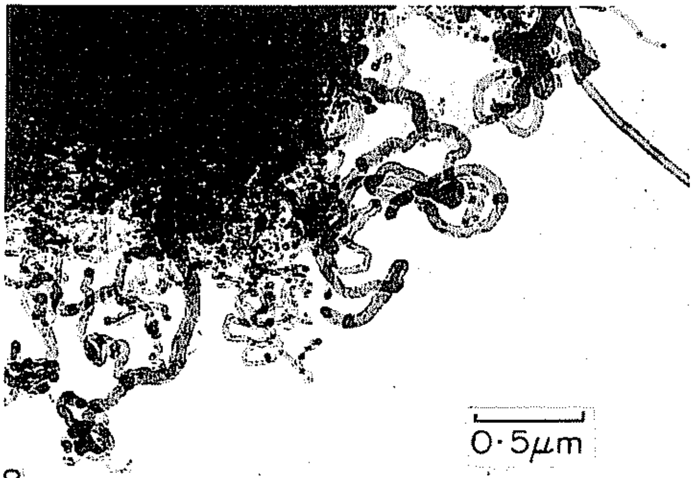

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Fig. 8. Filament formed when iron is heated in acetone at 500°C.

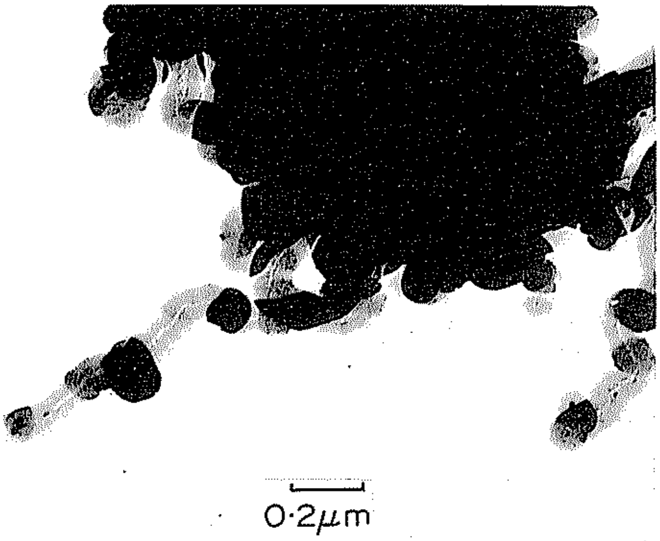

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Fig. 9. Filament formed on iron at 700°C in acetone. Note hollow core.

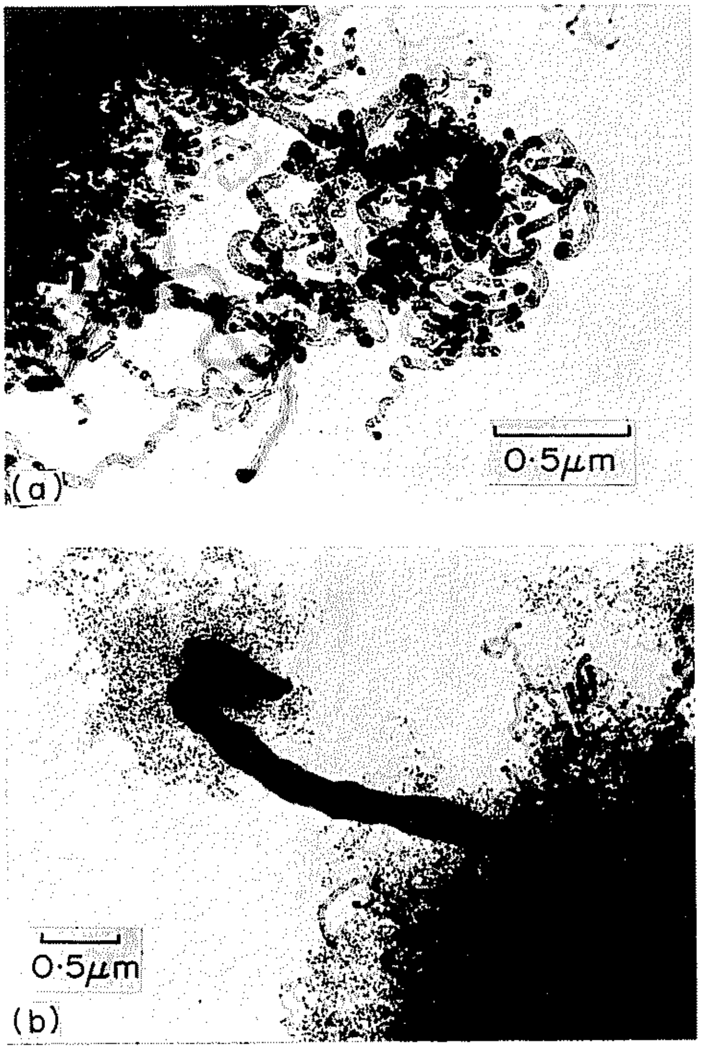

Fig. 10. Filaments formed when (a) stainless steel and (b) nickel are heated in acetone at 500°C.

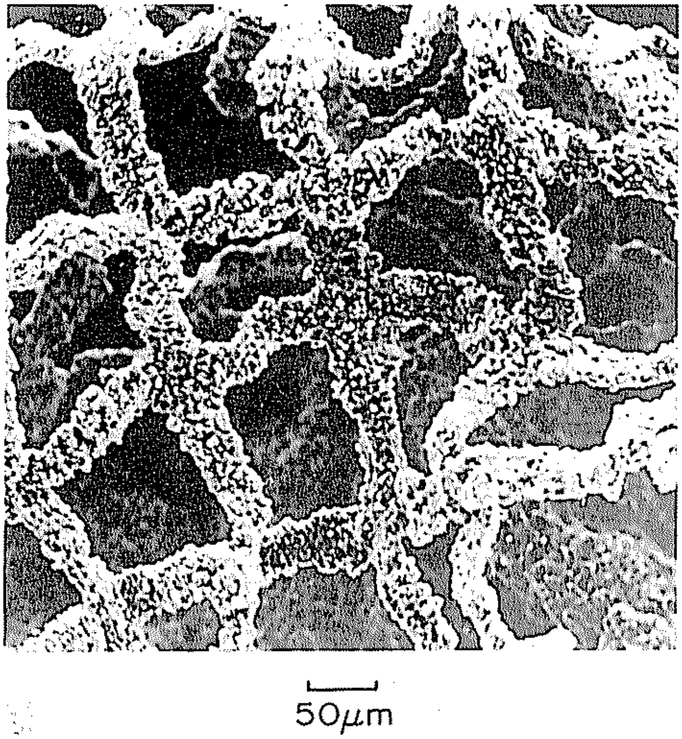

Fig. 11. Scanning electron micrograph of nickel grid after heating in acetone at 500°C.

(a) *Nickel*. Figure 4a shows the prolific formation of filaments achieved by heating nickel in methane at 900°C. High resolution studies of these particular filaments (Fig. 4b) revealed that they were less hollow than the corresponding stainless steel filamentary growths, and, in fact, there is some evidence to suggest that some contain numerous elongated, electron-dense particles along their cores.

Some platelet material was also observed on the fractured edge of the nickel grids after treatment at 900°C in methane (Fig. 5). Selected area electron diffraction of this region revealed that the platelet was graphitic with a much larger crystallite size than was observed for the carbon film formed on the stainless steel substrate.

(b) *Iron*. Iron heated in methane at 900°C also produced filaments, as shown in Fig. 6. This is particularly significant because it clearly shows that the fibres emanate from a main central stem. Presumably the catalytic particle responsible for growth of the original stem has fragmented to form new catalytic surfaces which promote further growth in all directions. Some of the filaments appear to have a narrow channel running along the core. Such channels could be escape paths for gases produced during the decomposition of the reacting species[7].

Some platelet formation was also obtained with iron.

3.2. *Acetone pyrolysis*

The fact that no filamentary growth was observed at temperatures below 900°C when ultra pure methane was employed in contrast to the filaments formed with commercial grade methane at temperatures as low as 500°C, would seem to indicate that trace impurities present in methane play a major part in the production of filaments at the lower temperatures. Since the reactions of most typical contaminant gases, such as CO and higher hydrocarbons, with metallic surfaces is well documented[2, 4], it was decided to investigate the effectiveness of another frequent impurity *viz.* acetone vapour, a material whose heterogeneous thermal decomposition does not appear to be so well characterized, in the formation of carbonaceous deposits.

Deposits were observed on all the metallic surfaces after exposure to acetone vapour at much lower temperatures than with methane.

3.2.1. *On iron*. Iron promoted deposit formation at 400°C (Fig. 7a), but there was no observable effect on either nickel or stainless steel at this low temperature. These deposits were lamellar in nature, and the dense regions observed were lamellae so oriented that the extended planes were parallel to the electron beam. This is revealed by tilting the sample through 25° and 50°, as shown in Figs. 7b and 7c, respectively. Selected area diffraction revealed that the deposit was polycrystalline γ-Fe_2O_3 identical to the acicular crystals of γ-Fe_2O_3 reported by Renshaw *et al.*[4], formed after reaction of iron with a CO/H_2 mixture at 550°C. There was no evidence of individual filament formation at this temperature.

Pyrolysis of acetone at 500°C, however, gave rise to formation of filaments, each filament associated with a dense particle at its tip (Fig. 8). No selected area diffraction patterns could be obtained from the tip material because the particles were too small and too dense for electron transmission. They are, however, undoubtedly the species responsible for filament growth by promoting the catalytic pyrolysis of acetone vapour.

Greater quantities of filaments were produced as the temperature was increased. There is evidence that some of the filaments formed at 700°C, have a narrow hollow core similar to the filaments formed from methane pyrolysis (Fig. 9).

3.2.2. *On nickel and stainless steel*. No observable effect was found on either nickel or stainless steel at 400°C when heated in acetone.

At 500°C, however, pyrolysis of acetone gave rise to filamentary growth similar to iron. Figs. 10a and 10b show stainless steel and nickel respectively. Nickel was by far the most efficient catalytic species, so much so in fact, that the original grids became extremely fragile under these conditions and underwent severe contortions as shown by the scanning electron micrograph (Fig. 11). At higher temperatures (550°C) reaction with nickel was so severe that the grid was completely converted to a highly flocculent matrix of interwoven filaments; and this matrix disintegrated into a light powdery material when disturbed. Neither stainless steel nor iron underwent such severe reaction.

4. DISCUSSION

4.1. *Methane*

The kinetics and mechanism of the thermal decomposition of methane have been studied for many years but the reaction is still incompletely understood[8]. It has been proposed [8] that the initial reaction in the homogeneous decomposition process is methyl (CH_3) and/or methylene (CH_2) radical formation but with the former being the most probable. The principal fate of the methyl radical is to form a uniform carbon deposit on the walls of the reaction vessel. Methane probably does not decompose efficiently on the walls or on this carbon deposit since it is so much more stable than CH_3, so that the carbon deposit is built up by CH_3 decomposition primarily. Palmer *et al.*[8] also propose an additional heterogeneous decomposition process involving nucleation of soot particles in the gas phase from decomposition of light hydrocarbons such as ethane, ethylene, and acetylene formed from secondary reactions of methyl and methylene radicals. Such soot particles are known to contain a large concentration of spin centres and, therefore, they present active surfaces for direct decomposition of methane. It may be feasible to propose a similar explanation for our observations, namely, that the platelet material results from decomposition of methyl radicals and/or the other light hydrocarbons on all surfaces and that the highly crystalline graphitic platelets are formed as a result of an epitaxial process at the surface of the metal[6, 9]. The filamentary growths are probably generated by decomposition of the same species although it is conceivable that methane itself could be decomposed directly to carbon at the active surface of the catalyst particle located at the filament tip.

4.2. *Acetone*

The homogeneous thermal decomposition of acetone has been extensively studied[10] but comparatively little work has been carried out on the heterogeneous process, or on the identification of the intermediate species involved in the reaction. A recent mass-spectrometric study[10], however, of the catalytic decomposition of acetone, showed that at least four intermediate species occurred in the gas phase during the course of the decomposition reaction, namely, two free radicals, CH_3 and CH_3COCH_2 and two negative ions CH_3^- and $CH_3COCH_2^-$. The principal stable products observed were CO and CH_4. The first step in the decomposition was formulated as

$$CH_3COCH_3 \xrightarrow{\text{surface}} 2CH_3 + CO,$$

followed by

$$CH_3 + CH_3COCH_3 \longrightarrow CH_4 + CH_3COCH_2.$$

Subsequent decomposition of the acetyl radical (CH_3COCH_2) could lead to ketene (CH_2CO) and subsequently light hydrocarbon formation

$$CH_3COCH_2 \longrightarrow CH_3 + \underset{\text{ketene}}{CH_2CO},$$

$$2CH_2CO \longrightarrow C_2H_4 + 2CO.$$

Carbon deposition from acetone could therefore follow similar paths to those formulated for methane *via* methyl radical and light hydrocarbon decompositions. In addition disproportionation of CO could be significant at the higher temperatures[4] and the presence of CO is responsible for the formation of γ-Fe_2O_3 with iron.

A mechanism for the growth of filamentary carbonaceous deposits from pyrolysis of acetylene has recently been postulated[7]. Small detached metallic particles act as catalytic surfaces for the 'exothermic' decomposition of acetylene to produce carbon which dissolved in and diffuses into the bulk of the metallic particle. Since decomposition and, hence, 'liberation' of heat occurs only at the leading tip of the particle, a temperature gradient is created along the particle with the colder zone at the base of the particle. Since the solubility of carbon in a metal is temperature dependent, precipitation of excess carbon will occur at the colder zone behind the particle, thus allowing the filament to grow. Such a process will continue until the leading tip of the catalyst particle is poisoned and filament growth will cease.

Since this mechanism is only applicable to exothermic decomposition reactions, and decomposition of methane is endothermic [11] it would appear at first sight that such a mechanism cannot be invoked to explain filamentary growth directly from methane pyrolysis. It must, therefore, be assumed that either there exists an alternative growth mechanism in the case of methane or, as is more probable, the filaments result from decomposition of secondary reaction products, such as light hydrocarbons, which undergo exothermic reactions.

5. CONCLUSIONS

1. It has been shown that the formation of filamentary carbonaceous deposits from pyrolysis of methane over metallic surfaces, such as iron, nickel and stainless steel, is dependent on the purity of the gas. No filaments are observed below a temperature of 900°C when ultra pure methane is pyrolysed, whereas temperatures above 500°C suffice to produce filaments from a commercial grade methane.

A typical contaminant, such as acetone vapour, could give rise to filamentary deposits at temperatures above 500°C, a nickel surface being an extremely efficient catalyst at such temperatures.

2. Platelet formation has been observed for both stainless steel and nickel, and in the case of nickel, pyrolysis of methane gives rise to well crystallized graphite.

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REFERENCES

1. Blake A. R., Hilton D. A. and Robins I. H., *J. Appl. Chem.* **17**, 321 (1967).
2. Palmer H. B. and Cullis C. F., *Chemistry and Physics of Carbon*, (P. L. Walker Jr. Ed.), Vol. I, p. 265. Marcel Dekker, New York (1965).
3. Robertson S. D., *Carbon* **8**, 365 (1970).
4. Renshaw G. D., Roscoe C. and Walker P. L. Jr., *J. Catalysis* **18**, 164 (1970); **22**, 394 (1971).
5. Karu A. E. and Beer M., *J. Appl. Phys.* **37**, 2179 (1966).
6. Robertson S. D., *Carbon* **10**, 221 (1972).
7. Baker R. T. K., Barber M. A., Harris P. S., Feates F. S. and Waite R. J., *J. Catalysis* **26**, 51 (1972).
8. Palmer H. B., Lahaye J. and Hou K. C., *J. Phys. Chem.* **72**, 348 (1968).
9. Presland A. E. B. and Walker P. L. Jr., *Carbon* **7**, 1 (1969).
10. Melton C. E., *J. Catalysis*, **5**, 234 (1966).
11. Palmer H. B. and Hirt T. J., *J. Phys. Chem.* **67**, 709 (1963).