

NUCLEATION AND GROWTH OF PYROLYTIC GRAPHITE FILMS ON NICKEL SUBSTRATES

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Surface oxide and surface crystallography were found to influence the microstructure and crystallinity of graphites prepared by pyrolysis of acetylene over heated Ni. Failure to remove surface oxide before pyrolysis leads to the formation of equi-axed graphite crystals; if oxide is removed by annealing *in vacuo* or hydrogen, a laminar film is formed. It was established that graphite can be grown epitaxially on the {110} faces of Ni, in preference to the {111} faces, although the latter are geometrically more favourable.

Introduction

The use of heated Ni as a substrate for the deposition of highly oriented graphite by pyrolysis of hydrocarbons is now well established through the work of Karu & Beer¹ and Presland & Walker.² The former authors stated that a prior anneal in a vacuum of 10^{-7} torr was necessary for the production of graphite; the latter carried out their pyrolyses over Ni pre-annealed in a vacuum of $\sim 10^{-5}$ torr. In both cases, the Ni surfaces used were polycrystalline rolled foils, and Presland & Walker² were unable to decide whether the growth of pyrolytic graphite in their system was epitaxial or not.

The experiments described in this paper were carried out in an attempt to answer two questions concerning the formation of highly oriented graphite in the Ni/acetylene system:

- (i) is a prior vacuum anneal necessary, and if so, why?
- (ii) is the growth process epitaxial?

Acetylene was pyrolysed over polycrystalline Ni foils with and without a prior vacuum anneal, and also after a prior anneal in a nitrogen/hydrogen mixture. Pyrolysis was also carried out over a single crystal of NiO.

Further experiments were carried out with single crystals of Ni as substrates, to determine whether the graphite deposits formed were epitaxial.

In all cases, the carbon deposits formed were characterised by optical microscopy and conventional and scanning electron microscopy.

Experimental

The pyrolysis system employed was similar to that used by Presland & Walker² and Blau & Presland.³ Polycrystalline foils were heated by direct passage of current, while the Ni and NiO single crystals were heated on a tantalum boat.

Single crystal Ni samples with {110} and {111} faces were prepared by sawing from a single cylindrical crystal, oriented with a $\langle 110 \rangle$ zone axis along the axis of the cylinder. After sawing, the working faces of these crystals were polished on 0000 Grade SiC paper and finally electropolished.

The NiO single crystal was prepared by chemical vapour deposition on to cleaved MgO; its surface was parallel to {001}.

The acetylene pressure used was always the same, nominally 0.5 torr, as measured with a thermocouple gauge calibrated against a McLeod gauge.

Pyrolysis was carried out for 30 minutes at 1000° over the polycrystalline foils and the NiO. Since the single crystal Ni substrates were used to study the nucleation and early stages of growth of the graphite, pyrolysis times were short (2 minutes at 1000°). Even so, this was sufficient to produce complete coverage of the substrate in almost all cases.

Carbon deposits were examined *in situ* by optical microscopy. Half of each deposit was then coated with gold for scanning electron microscopy, while the remainder was stripped in HCl and washed and mounted for transmission electron microscopy.

Results

Effect of surface oxide

Fig. 1 shows a micrograph of the graphite deposit obtained on a polycrystalline foil, after pyrolysis for 30 minutes at 1000°. The fact that both laminar and nodular graphite are present indicates that the pressure was probably nearer 0.4 than 0.5 torr,³ but otherwise this deposit is similar to many others that have been obtained using Ni foils pre-annealed in a vacuum of 10^{-5} torr or less.

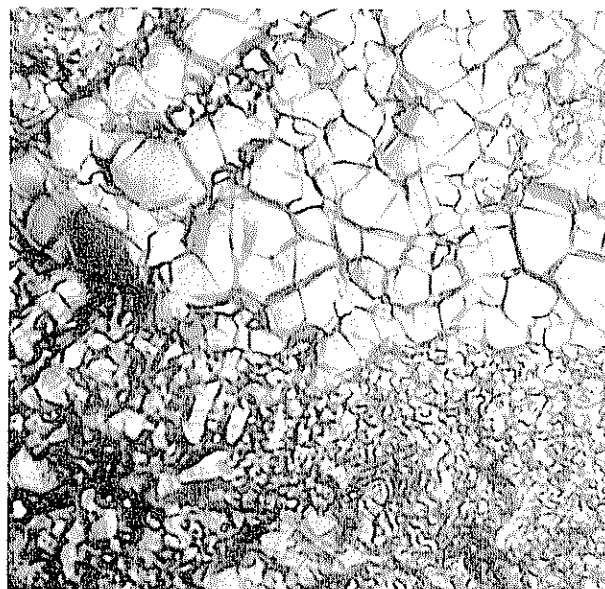


Fig. 1. Mixture of laminar and nodular graphite formed over vacuum-annealed polycrystalline Ni, $\times 700$

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The same pyrolysis carried out on a foil which had received no vacuum anneal after chemical cleaning gave a very different result. Optical microscopy appeared to show the presence of columnar growths of graphite, but the scanning electron microscope exposed the true morphology. Graphite was, in fact, still deposited, but in the form of roughly equi-axed, faceted, boulder-shaped crystals (Fig. 2). A selected area diffraction pattern from an extraction replica taken from this surface confirmed that these crystals were graphite.

Next, a Ni foil was pre-annealed at 1000° for 15 minutes in an atmosphere of 95% N₂/5% H₂ at 0.5 torr. Subsequent pyrolysis again produced a mixed deposit of

both laminar and nodular graphite; Fig. 3 shows the laminar graphite. Two new features were observed: bright patches, which corresponded to regions where the Ni substrate could be seen through holes in the overgrowth, and dark areas, which were shown by scanning electron microscopy to be depressions in the graphite (Fig. 4).

The single crystal of NiO was then used as a substrate. After pyrolysis for 30 minutes at 1000°, the NiO appeared, under the optical microscope, to be covered with a fine speckling of carbon particles (Fig. 5); in general these were randomly distributed, but some dark lines parallel to $\langle 100 \rangle$ directions could be seen.

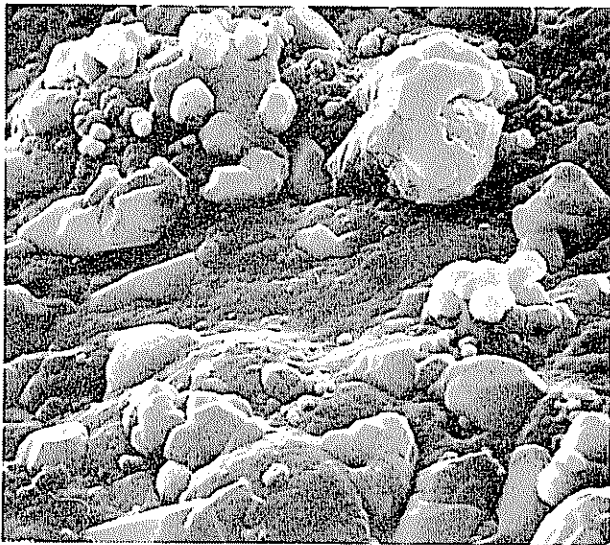


Fig. 2. Faceted graphite crystals formed over unannealed Ni, $\times 480$

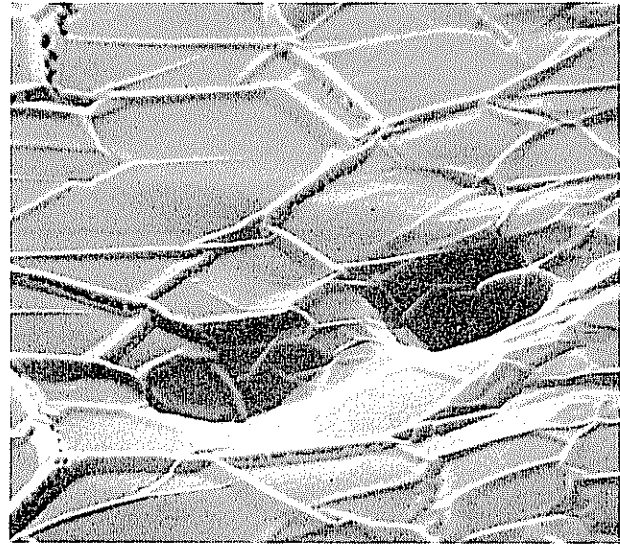


Fig. 4. Depressions in laminar graphite, $\times 10,000$

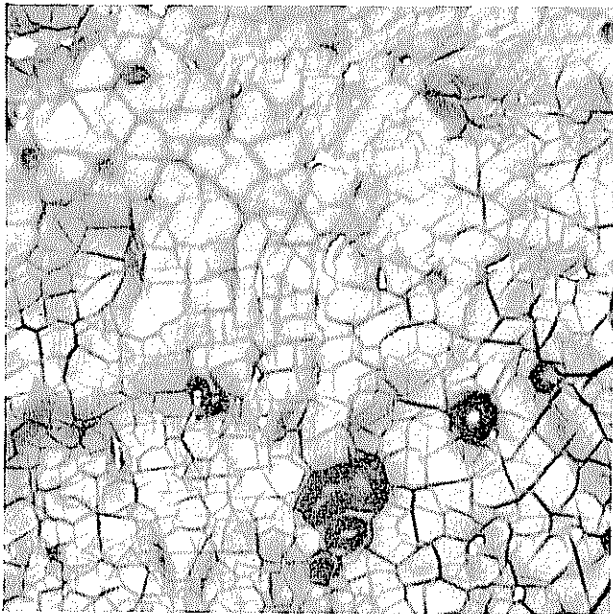


Fig. 3. Laminar graphite formed over hydrogen-annealed Ni, $\times 700$

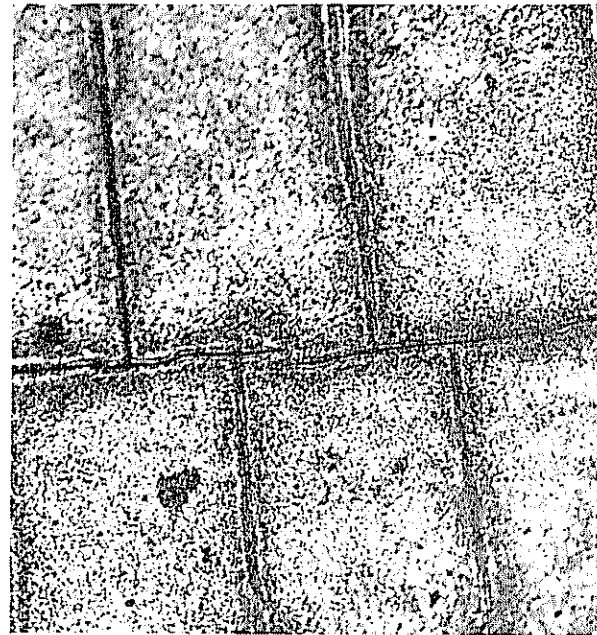


Fig. 5. Optical micrograph of NiO after pyrolysis, $\times 640$

Electron probe micro-analysis confirmed that these linear features were relatively rich in carbon, but the C K_{α} signal obtained was very weak (only slightly greater than the noise level). This result was explained when the NiO was examined by scanning electron microscopy. The surface was extensively pitted (Fig. 6) and the dark lines were shown to be deep cracks in the oxide. Some of the contrast in the optical micrographs of the NiO must therefore have been due to low reflectivity caused by trapping of the incident light within the pits and cracks; the weak C K_{α} signal may indicate either that very little carbon was produced over the NiO or that it was formed deep in the pits.

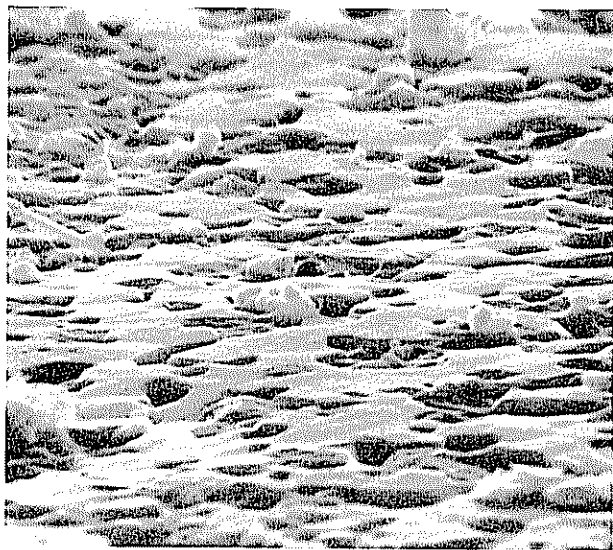


Fig. 6. Pits in NiO after pyrolysis, $\times 18,000$

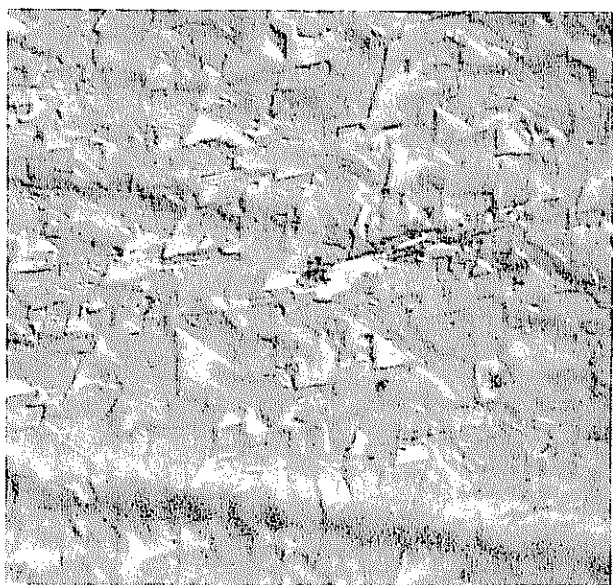


Fig. 7. Triangular platelets of graphite formed over single crystal Ni, $\times 700$

Effect of surface crystallography

Deposits of variable morphology were also produced on the single crystal Ni substrates, probably because the acetylene pressure was too high to permit the formation of laminar graphite only. Both the (111) and (110) faces of Ni formed irregular nodular graphite, together with areas of regular, usually triangular, platelets (Fig. 7).

Transmission electron microscopy of these deposits, however, showed that regularity of morphology was not an accurate indication of perfection of structure. Thus, individual triangular platelets stripped from the (111) surface of Ni gave selected area diffraction patterns which were polycrystalline (Fig. 8). Conversely, the thin,



Fig. 8. Selected area diffraction pattern from a single graphite platelet deposited on (111) Ni

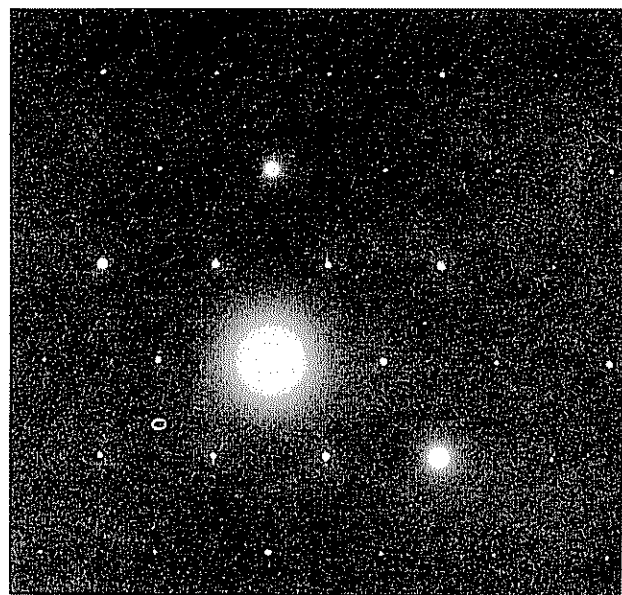
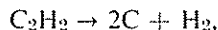


Fig. 9. Selected area diffraction pattern from graphite formed on (110) Ni

rather featureless, platey deposits from the (110) surface of Ni gave excellent single crystal diffraction patterns (Fig. 9); in some cases, these single crystal areas were as large as 50 μm across. Spot patterns of this type were never obtained from the (111) specimens.

Discussion

It seems clear that the main function of a pre-anneal in high vacuum is to remove surface oxide, which acts as an inhibitor for the formation of laminar graphite. NiO may, in fact, be an inhibitor for the formation of pyrolytic carbon of any type, and it would be of interest to compare the rate of deposition of carbon on NiO with that on metallic Ni. There are two aspects to this. Ni may be a much better catalyst than NiO for the overall reaction:

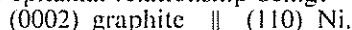


and such carbon as is formed on NiO may be less ordered than that on Ni as a result of its lower mobility on the NiO.

The formation on unannealed Ni foil of well ordered graphite in the form of separate crystals rather than sheets of laminar graphite can now be explained. Such a foil would be covered with a layer of NiO. The results obtained with pure NiO showed that pyrolysis in acetylene would lead to the formation of etch pits, and when these etch pits reached the Ni surface, the latter could act as a substrate for the nucleation and growth of laminar graphite. Lateral growth would be limited by the walls of the etch pit, but it could grow in a direction normal to the surface, until the crystal eventually appeared above the oxide. There are indications in Fig. 2 that some of the graphite crystals are emerging from holes in the underlying oxide.

Pre-annealing in a nitrogen/hydrogen mixture is also an effective method of removing surface oxide to permit the formation of laminar graphite. The holes and depressions in the graphite overgrowth may, however, indicate that the hydrogen anneal used was insufficient to clear the surface completely of oxide.

The pyrolyses carried out over single crystal substrates indicate that epitaxial growth can take place over {110} surfaces, the epitaxial relationship being:



The directional relationship has not yet been established.

It is surprising that epitaxy does not occur over (111) Ni, since the geometry is considerably more favourable, as shown in Fig. 10. Both (0002) graphite and (111) Ni have hexagonal symmetry, and if they are arranged with [10 $\bar{1}$ 0] graphite \parallel [112] Ni, the fit along

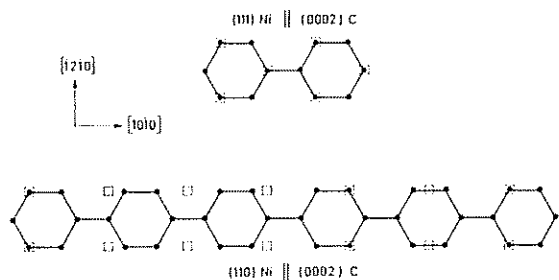


Fig. 10. Possible epitaxial relationships between (0002) plane of graphite and (111) and (110) planes of Ni

● C atoms; □ Ni atoms

both the [10 $\bar{1}$ 0] and [$\bar{1}$ 2 $\bar{1}$ 0] directions in the basal plane of graphite is better than 1½%.

In the case of (110) Ni, however, the situation is different. If this plane is fitted to (0002) graphite, with [001] Ni \parallel [10 $\bar{1}$ 0] graphite as in Fig. 10, it is found that agreement to 1½% is achieved perpendicular to [10 $\bar{1}$ 0], i.e., along [$\bar{1}$ 2 $\bar{1}$ 0], since for graphite $a = 2.46 \text{ \AA}$, while for Ni $a_0 = 3.524 \text{ \AA}$, so that the relevant spacing $a_0/\sqrt{2} = 2.49 \text{ \AA}$. But along the [10 $\bar{1}$ 0] direction in graphite, the periodicity of fit is much greater. Thus $6a_0(\text{Ni}) = 21.144 \text{ \AA}$, while $5(\sqrt{3}a)(\text{graphite}) = 21.315 \text{ \AA}$, the difference being 0.171 \AA , or less than 1%.

The most important crystallographic parameter here is probably the metal atom spacing, $a_0/\sqrt{2}$, along the $\langle 110 \rangle$ directions. For Ni, this is 2.49 \AA , which should be compared with a , the C—C separation along $\langle 11\bar{2}0 \rangle$ graphite, which is 2.46 \AA . Since all (111) planes in Ni contain a $\langle 110 \rangle$ direction, it is possible that they all have some potentiality for inducing graphite epitaxy. Further, the spacing along [110] in a f.c.c. metal depends upon a_0 , and it would be of interest to compare different f.c.c. metals from this point of view.

A complicating factor is that different lattice planes in the substrate may also give rise to different pyrolysis rates, thus affecting the carbon supersaturation. Thus, in these experiments there seemed to be qualitative evidence that the rate of formation of carbon was greatest over (111), which may have been sufficient to offset the apparent geometrical advantage of this plane. Alternatively, 1000° may have been within the epitaxial range for {110} Ni, but too high for epitaxy on {111}.

Finally, it must be admitted that the presence of both laminar and nodular graphite on the same substrate crystal plane indicates that the nucleation density is non-uniform, the reasons for which are not yet clear. It is known that the step and terrace structure of the Ni surface has a large influence here.²

Conclusions

- (1) The deposition of ordered laminar graphite by pyrolysis of acetylene over Ni can occur only when the Ni surface is substantially free of oxide.
- (2) When surface oxide is present, graphite may be formed in limited quantities, but the morphology is quite different; roughly equi-axed, faceted crystals are produced.
- (3) It is possible that the ordered laminar graphite deposited on polycrystalline Ni grows by an epitaxial process, since epitaxy has been shown to occur on the {110} planes of Ni.
- (4) At 1000°, the {110} planes are more effective than {111} planes as far as epitaxy is concerned, although the geometry of the {111} planes appears to be more favourable.

Acknowledgments

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References

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DISCUSSION

Prof. J. M. Thomas (Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth):—Quite apart from the importance of faceting (which often commences preferentially at emergent dislocations) in determining the extent of overgrowths, oriented or otherwise, there is also the phenomenon of surface reconstitution, as revealed by low energy electron diffraction of metal surfaces. It must not be concluded that (110) and (111) faces, in vacuum or in the presence of a variety of gases, have the structure expected from the results of X-ray diffraction. There are a variety of surface configurations possible.

Dr. H. M. Montagu-Pollock (Dept. of Physics, University of Lancaster):—With regard to your interest-

ing conclusions about epitaxy of graphite, some low energy electron diffraction studies by Ertl ('Molecular Processes on Solid Surfaces', (Gretz, *et al.* Eds) 1969 (New York: McGraw-Hill)) are relevant. Some field emission studies by Whalley (personal communication) at Warren Spring Research Laboratories should also be mentioned, involving work on the dissociative adsorption of acetylene and ethylene on nickel. He found that dissociation took place preferentially on nickel surface planes such as (112) and (113) with their terrace plus step structure. If the substrate was subsequently heated, crystallites of carbon appeared on planes adjacent to (110).