PYROGENICS, INC. 25-26 50th STREET • WOODSIDE, NEW YORK 11377

A Study of the Use of Vapor and Vacuum Deposition Technique For The Development Of High Strength Filamentary Materials

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ABSTRACT

An original approach to the deposition of pyrolytic graphite thin films using a liquid metal substrate is described. The advantages of using such a substrate and the factors influencing the choice of substrate material are discussed.

Initial attempts to deposit on molten platinum were unsuccessful due to a reaction between the substrate and the deposited graphite. Using a molten gold substrate, however, and depositing from methane using argon at a pressure of 50 cms Hg as a carrier gas, a number of successful deposition experiments were carried out.

Some subsidiary experiments on the use of solid metallic substrates are described and discussed.

I. INTRODUCTION

The theoretical yield stress for a perfect crystal can be estimated by considering the shearing of two rows of atoms past each other, in a homogeneously strained crystal, as in Figure 1a. Let 'a' be the spacing between the two rows, and let 'b' be the distance between atoms along the slip direction. The equilibrium shear stress σ to hold the plane at a distance x is zero at the initial and final positions (A and B), and also at positions halfway between them, by symmetry (i.e. at $x = 0$, $x = b/2$, and $x = b$). The shearing force must be a periodic function of x, with period b, and if it is assumed that it is sinusoidal, as in Figure 1b, then

$$\sigma = \sigma_{max} \sin \frac{2\pi x}{b} \qquad \text{-------(1)}$$

For small values of x, Hooke's law should apply:

$$\therefore \sigma = G \frac{x}{a} \qquad \text{------(2)}$$

Where G is Young's Modulus.

Since $a \simeq b$, and, for small x, $\sin x \simeq x$

$$\text{Then } \sigma_{max} \simeq \frac{G}{2\pi} \qquad \text{------(3)}$$

It has been estimated that the polarizability or deformability of the atoms may reduce the value by a factor of about 5, (Birchenall, 1959) giving

$$\sigma_{max} \simeq \frac{G}{30}$$

Substituting experimentally determined values of G gives a calculated yield stress of the order of 10^6 psi for high strength metals, and values ranging up to approximately 5×10^6 psi for some non metallic fibres. These values are of course orders of magnitude greater than even the strongest bulk material known.

It is thus impossible to produce slip in a perfect crystal under the small stress at which real crystals begin to slip. However, the calculation of the theoretical stress is made for the homogeneous shearing of two rows of atoms across each other. In practice, this is not the case, and shearing in a real crystal actually takes place by a nucleation and growth type process in which slip starts at localized regions in the lattice and then spreads gradually over the remainder of the slip plane. The boundary between the slipped and unslipped region is a dislocation.

Plastic deformation is brought about by moving dislocations. It is apparent, therefore, that there are two ways by which a material can be strengthened. These are:

1. By the removal of dislocations from the particular lattice, and

2. By putting obstacles in the way of dislocations, and so prevent their moving by the pinning action of the obstacle.

Effective strengthening by the first of these can be achieved in two ways, both of which involve the production of specimens with a high surface area to volume ratio.

Because of their unique method of growth, single crystal whiskers having diameters less than approximately 12 μ contain a very small number of dislocations, and in the ideal case only one screw dislocation. These whiskers have been shown to have strengths many times that exhibited by the bulk material. For example, Brenner (1956) demonstrated that copper whiskers had yield strengths up to approximately 9×10^4 psi compared with 2×10^3 psi in the bulk material. In addition to whiskers, polycrystalline thin films of copper (less than 10μ thickness) have been shown to have strengths up to an order of magnitude greater than those exhibited by the bulk material, Lawley and Schuster, (1964). Similar effects have been observed in copper fine wires having diameters less than 100μ Hughes, Johnson and Barton, (1964, 1965). The reasons for these effects are somewhat obscure, but it is believed that it is due to either dislocation pinning at the surface or the small number of dislocations present due to the small volume of the specimens, or possibly, a combination of the two.

The second method of strengthening materials i.e. by obstructing the passage of dislocations is by far the most commonly used method

of strengthening. This can be achieved by using polycrystalline materials in which the grain boundaries obstruct dislocation movement and cause dislocation pile-ups. Further strengthening can be obtained by cold working the material i.e. causing dislocations to intersect and effectively prevent further movement. In addition to the above two methods of dislocation pinning which apply both to pure materials and alloys, the dislocations can also be pinned by impurity atoms in the lattice. Thus by alloying two metals, or one metal with a non metal, additional strengthening can be obtained. In the former case, hardening is usually termed solid solution hardening, or in certain alloys, after the appropriate heat treatment, precipitation hardening. In the latter case, it is usually caused by the smaller non metallic atoms positioning themselves in the interstices between the metal atoms, resulting in dislocation pinning and so called interstitial hardening.

The method of approach adopted in the present work has been to take the material, which on the basis of its Young's Modulus should theoretically have the highest yield strength (see Equation 3), and to attempt to produce this in a form which should further enhance its strength. Graphite, which in whisker form has the highest reported modulus of all materials (145×10^6 psi) Bacon, (1960) was therefore

chosen as the material to investigate. In order to obtain the highest possible strengths, it was decided to produce the graphite in the form of thin films or fibres.

Carbon can exist in a number of allotropic forms ranging from disordered amorphous carbon at one extreme to the highly ordered graphite structure at the other. Intermediate between these two extremes is pyrolytic graphite which consists of an aggregate of crystals slightly misoriented with respect to each other. Pyrolytic graphite, which is formed by depositing from the vapor phase at temperatures between 1700°C and 2300°C consists of layers of wavy and kinked hexagonal planes parallel to each other, but randomly rotated about an axis perpendicular to the plane of the deposit. This axis is known as the 'c'axis or direction, and the direction parallel to the planes is the a-b direction. Pyrolytic graphite has many properties which can make it an ideal material for many high temperature applications. These include increasing strength with increasing temperature, a high degree of anisotropy which results in high thermal and electrical conductivities in the ab direction and low conductivities in the c direction. Other properties include high strength to weight ratio and a low vapor pressure.

II. PRELIMINARY EXPERIMENTS

The properties of pyrolytic graphite are extremely sensitive to a number of variables, the most important of which are listed below:

1. Substrate temperatre.
2. Gas pressure.
3. Gas flow rate.
4. Substrate material and perfection.

Most of the past work has been concentrated on the first three of the above variables, e.g. Higgs, Finicle, Bobka, Seldin and Zeitsch, (1964), Bradshaw and Armstrong, (1963) and a minimum amount of work has been carried out on the effect of substrate material Diefendorf, (1960). The approach adopted in the present work was therefore primarily to investigate the effect of substrate material on the mechanical properties of pyrolytic graphite thin films and fibres.

In the past, pyrolytic graphite deposition has always taken place on a solid substrate material. In the present work a completely new approach was taken and the main effort was concentrated on developing a liquid substrate. The possible advantages to deposition on a liquid surface are:

1. Freedom from stresses which may be introduced into the film as a result of the differential contractions on cooling.

2. By virtue of its superficial perfection, the liquid surface should be non-nucleating and may permit continuous growth from a single seed.

3. Since the deposit should not adhere to the substrate, ready and easy removal should be possible. This, of course, is extremely important should the production of continuous filaments be desired.

In addition to the development of a liquid substrate, some subsidiary experiments were carried out to investigate solid metallic substrates. These experiments are described in Appendix I.

II.1 Choice of Substrate Material

The choice of liquid metal to be used was at first limited to those with melting points between approximately 1800°C and 2400°C which is the temperature range over which pyrolytic graphite is usually deposited. Another factor which was considered was the vapor pressure of the liquid metal over this temperature range. Ideally, this should be as low as possible in order to reduce excessive loss of the substrate material due to vaporization. From these two considerations alone, a

survey of the available data on the melting points and vapor pressures of metals indicated that the most suitable materials from these points of view were palladium, platinum, titanium, zirconium and vanadium. However, the choice was further restricted when the chemical reactivity of the above elements with carbon was considered. Any chemical reaction of the carbon formed from the dissociated methane with the liquid substrate will inhibit the formation of a pyrolytic deposit. With the exception of palladium and platinum, all of the above metals react with carbon to form carbides, and the choice of liquid substrate was therefore limited to these two metals. The final choice, purely on the basis of economic considerations, was platinum.

II.2 Experimental Procedure

In the initial attempts to deposit pyrolytic graphite on molten platinum, the latter was contained in a small graphite boat which was heated directly between two water cooled copper electrodes. The methane pressure was measured by means of a Dubrovin pressure gauge. A schematic drawing of the reaction vessel is shown in Figure 2 and Figure 3 is a photograph of the complete assembly. The temperature of the substrate was measured by sighting an optical pyrometer on the metal through a glass prism. (See Figure 2). The necessary corrections for emissivity and window absorption were made. In a typical run the apparatus was first evacuated to a pressure of 10^{-2}mm Hg, and

the specimen was slowly raised to temperature by increasing the current. When the specimen was at the required deposition temperature, a continual flow of methane at the desired pressure was admitted to the reaction vessel. The run duration was usually one hour.

In many of the runs, deposition was for less than one hour, usually because of irregularities in the functioning of the apparatus. One of the major reasons for this was large and unpredictable changes in specimen temperature. These were usually due to the tantalum heat shield (see Figure 2) expanding to touch both electrodes and causing a short circuit.

?

What high school freshman would be doing this job?

III. EXPERIMENTAL RESULTS AND DISCUSSION

Table 1 is typical of the results obtained in the early experiments. In this particular run a substrate temperature of 2200 ± 40°C was maintained throughout the run. The deposit obtained was found to adhere to the substrate, and a massive reaction between the liquid platinum and the graphite boat was observed.

A section taken through the platinum button was mounted, polished, and examined metallographically. The examination revealed that the button contained massive graphite flakes, and on the surface, a thin layer of graphite covered with a pyrolytic graphite deposit was observed (Figure 4). It appeared from the micrographs that the liquid platinum had dissolved carbon from the graphite boat or from the dissociated methane, and on cooling the carbon came out of solution in the form of massive graphite flakes.

In an attempt to prevent the carbon from the boat going into solution in the platinum, the graphite boat was replaced by a pyrolytic graphite boat oriented so that the 'c' axis would be exposed to the molten platinum. Since the 'c' direction in pyrolytic graphite is impervious to gases and, in many cases, not attacked by acids and liquid metals, it was thought that the reaction between the molten platinum and the boat may be prevented. However, after melting the platinum in the pyrolytic graphite boat, a reaction was still observed.

Following the unsuccessful attempts to use graphite as a container material, it was decided to use zirconia, a material which is not susceptible to attack by liquid platinum. Due to the fact that zirconia is an insulator, direct heating could not be used. Induction heating was therefore used to melt the platinum which was contained in a zirconia crucible 1/2 inch in diameter and 1/2 inch in height. A schematic drawing of the apparatus is shown in Figure 5. The crucible was supported on a graphite block which in turn was supported on a graphite rod set into a water cooled brass end piece. The whole specimen assembly was contained in a quartz tube which could be evacuated to a pressure of 10^{-2} mm Hg. The temperature was measured by a disappearing filament pyrometer sighted through a prism situated vertically above the specimen (Figure 5). In the early deposition experiments carried out in this apparatus, difficulty was experienced due to the zirconia crucibles fracturing from thermal shock during the heating and cooling cycles. However, a sufficient number of successful deposition experiments were performed to demonstrate that a reaction still occurred between the platinum and the deposited film. At this stage of the program it was therefore decided to discontinue the attempts to deposit pyrolytic graphite on liquid platinum.

IV EXPERIMENTAL METHOD II

While a high melting point and low vapor pressure are most advantageous properties in a material which is to be used as a liquid substrate, it is not essential that a substrate should have these properties, provided that vaporization of the substrate can be reduced to a minimum. With this in mind, the choice of substrate was reconsidered, and it was decided to base the choice entirely on the lack of any reaction with carbon. From this point of view, two of the most promising materials are gold and copper.

The initial experiments were carried out with a liquid gold substrate in the apparatus shown in Figure 5. Since molten gold does not react with graphite, graphite could be used as the crucible material, thus eliminating the difficulties previously encountered with the zirconia crucibles. Approximately five gms of gold were melted under an argon atmosphere in an ATJ graphite crucible. The argon was pumped continuously through the reaction vessel and a constant pressure of 50 cms Hg was maintained. The temperature of the gold was raised to 2160±40°C and methane was admitted to the system at a pressure of 5 cms Hg. These conditions were maintained for a period of fifteen (15) minutes after which the methane flow and the power were cut off. During the experiment some vaporization of gold was observed, but immediately deposition commenced, there

was no further vaporization. This effect was presumably due to the graphite film inhibiting the gold vaporization.

V. EXPERIMENTAL RESULTS AND DISCUSSION II

When the specimen had cooled to room temperature the crucible was removed from the apparatus and the specimen examined. Figure 6a shows the crucible together with the deposited film as they appeared on removal from the apparatus. The smooth appearance of the film surface can be clearly seen. The film did not adhere to the gold substrate and could easily be removed by using Scotch tape. The deposited film was smooth in appearance on both the upper and lower surfaces. This is illustrated in Figures 6b and 6c where both surfaces are shown after removal from the substrate. A section perpendicular to the growth direction was taken through the strip and was examined metallographically under polarized light. The metallographic examination revealed that the deposited film had a continuously nucleated pyrolytic structure. This structure is illustrated in Figures 7a and 7b where the typical pyrolytic structure is clearly visible.

The results of the preliminary deposition attempts on liquid platinum proved unsuccessful, mainly because of the graphite both from the crucible and the film going into solution in the platinum. The decision to use platinum had been based mainly on its high melting point of 1769°C and low vapor pressure of less than 10^{-2}mm Hg at this temperature. However, the results obtained demonstrated that both these factors were outweighed by the chemical reactivity of the graphite film with the substrate.

The preliminary experiments carried out with gold demonstrated that in spite of its comparatively high vapor pressure of approximately 10 mm HG at the deposition temperature (2160°C), a smooth pyrolytic graphite film deposit could be obtained. Furthermore, once deposition had commenced, there were no more visible signs of vaporization. It appears, therefore, that pyrolytic film deposition on a liquid substrate is quite feasible.

Although the actual physical process of deposition on a liquid substrate has been achieved, it still remains to investigate the effect of the many deposition variables on the mechanical properties of the deposited film. In addition, other liquid materials will be tried as substrates. The most promising of these materials from the point of view of chemical reactivity is copper. Furthermore, many of its properties e.g. melting point and vapor pressure, are similar to those of gold. One of the most important advantages of replacing gold by copper would be from the economic viewpoint. As well as attempting to deposit on liquid gold, it may be advantageous to investigate the possibility of using a gold-rich alloy as a substrate material.

In addition to the economic advantage of such a substrate, by choosing a suitable alloying element, it should be possible to reduce the vaporization of the substrate at temperatures between the melting

point and the deposition temperature. Ideally, the element chosen should form a solid solution with gold, have a high melting point, and a low vapor pressure. The type of substrate will, of course, affect the mechanical properties of the deposited film, and it will therefore be necessary to determine the effect of the substrate material on these properties. This can best be accomplished by mechanically testing a series of films deposited on different substrates under identical deposition conditions.

VI. CONCLUSIONS

In the first year of the contract, it has been demonstrated that the deposition of a pyrolytic graphite film on a liquid substrate is entirely feasible. The main controlling factor in the deposition experiments was the chemical compatibility of the graphite film with the liquid substrate. For this reason, liquid platinum, which from the melting point and vapor pressure points of view is ideal, was shown to be unsuitable. The substrate with which most success was obtained was liquid gold. However, further experiments must be carried out to test the possibility of using other liquid substrates such as copper, or a gold-rich alloy, before a final choice of substrate material is made.

The success so far achieved with a liquid metal substrate is most promising from the point of view of developing a continuous process for the production of thin films or fibres. Such a process would, of course, be a significant advance in the art of pyrolytic graphite technology.

VII FUTURE WORK

In the immediate future, the major effort will be centered on examining the effect of deposition variables on the film strength.

This part of the project is already under way and films are now being deposited systematically at a series of different temperatures

and methane pressures. These deposited films will be ultimately tested in tension in order to determine the optimum deposition conditions in terms of these two variables. In addition, the effect of film thickness on the tensile strength is under investigation, and for each temperature and pressure, the deposition time will be varied so as to produce films covering a fairly large range of thicknesses.

ACKNOWLEDGMENTS

The author is indebted to Dr. W. Robba for many helpful discussions and suggestions. He also thanks Mr. J. Bedell who was responsible for all of the early work on the molten platinum substrate and also for the work on the iridium substrate described in the Appendix. Thanks are also due to Mr. E. Ashton who helped with the experimental work.

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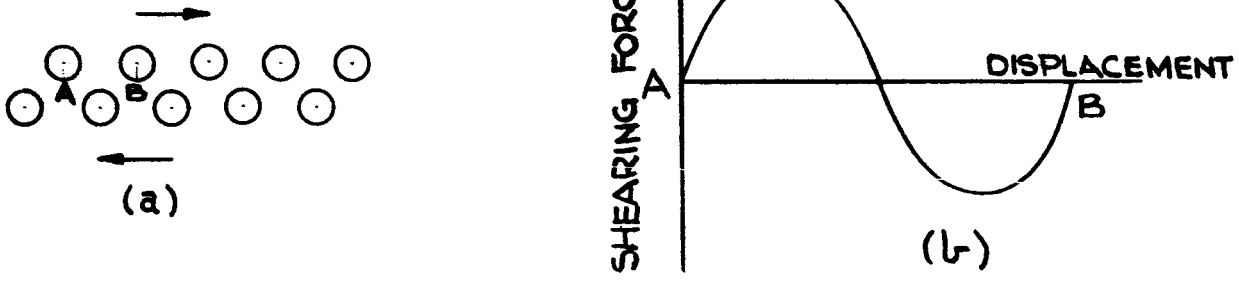


FIG. 1

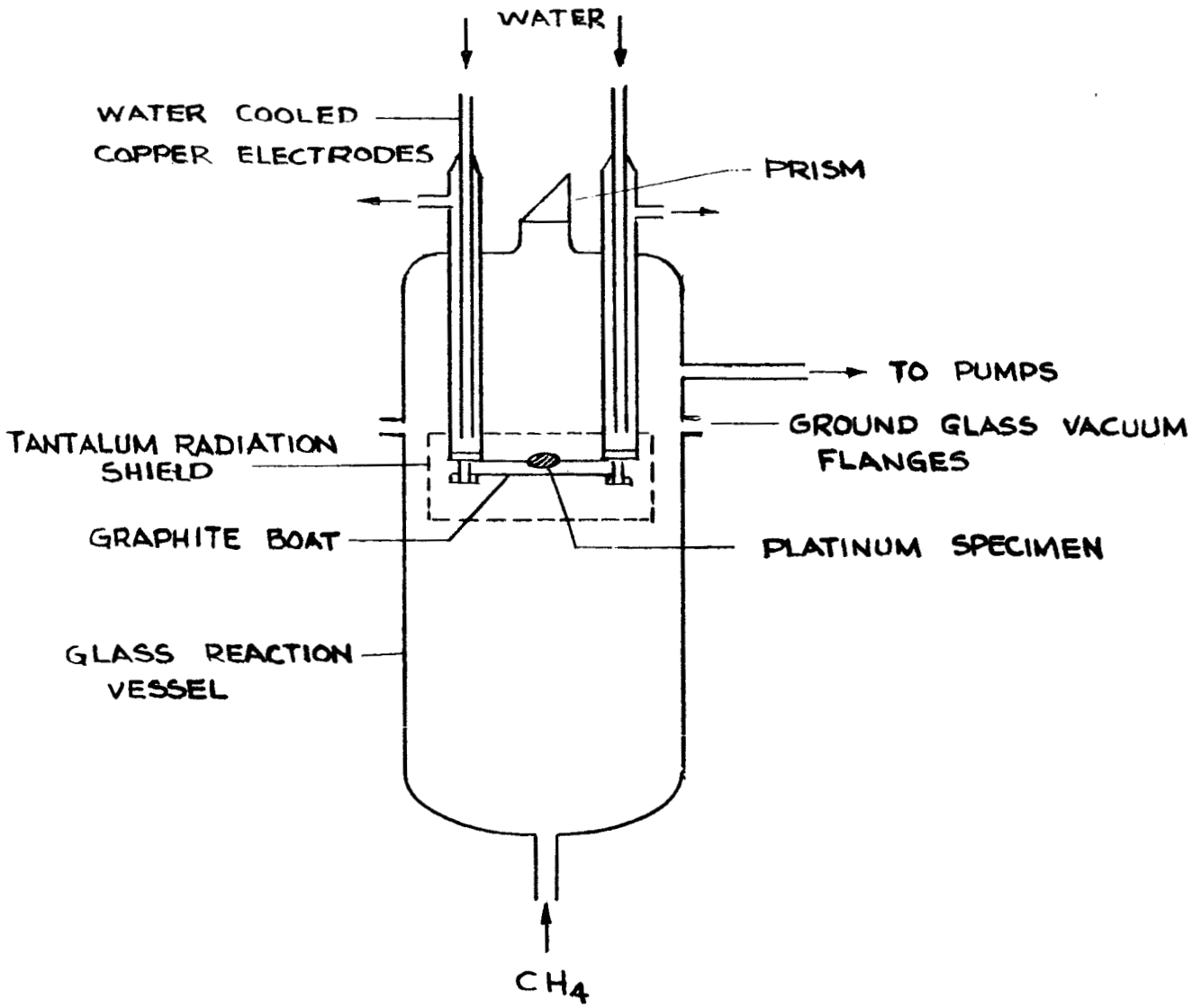


FIG. 2 SCHEMATIC DRAWING OF GLASS REACTION VESSEL FOR PYROLYTIC GRAPHITE FILM DEPOSITION

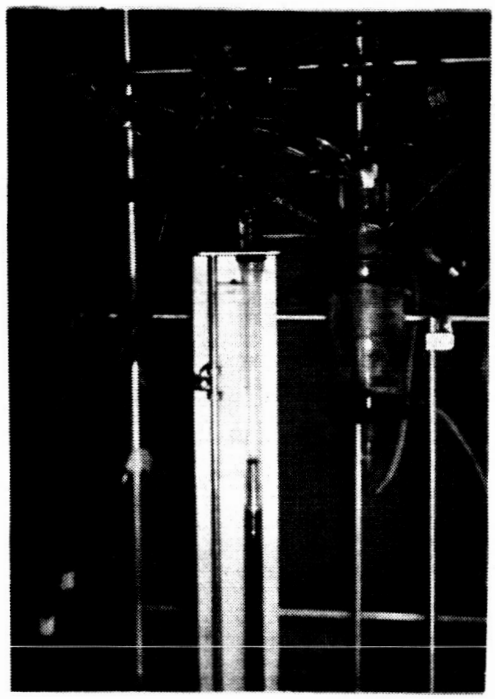


FIG. 3 PHOTOGRAPH OF GLASS REACTION VESSEL

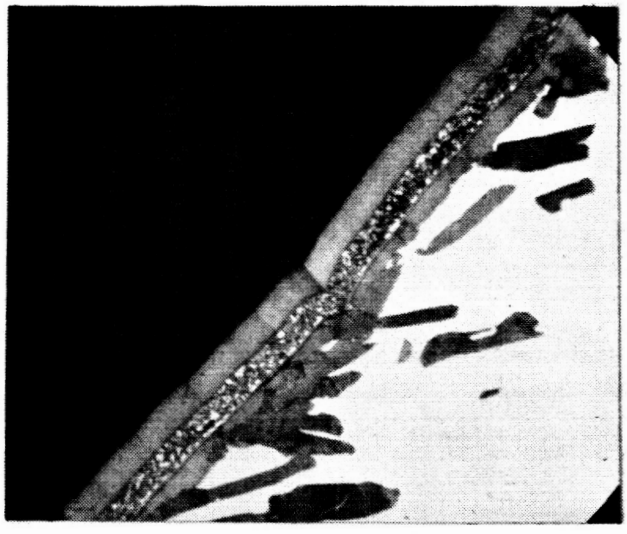


FIG. 4 SECTION THROUGH PYROLYTIC GRAPHITE DEPOSIT ON LIQUID PLATINUM SHOWING SURFACE LAYER OF GRAPHITE AND MASSIVE GRAPHITE FLAKES (X 400)

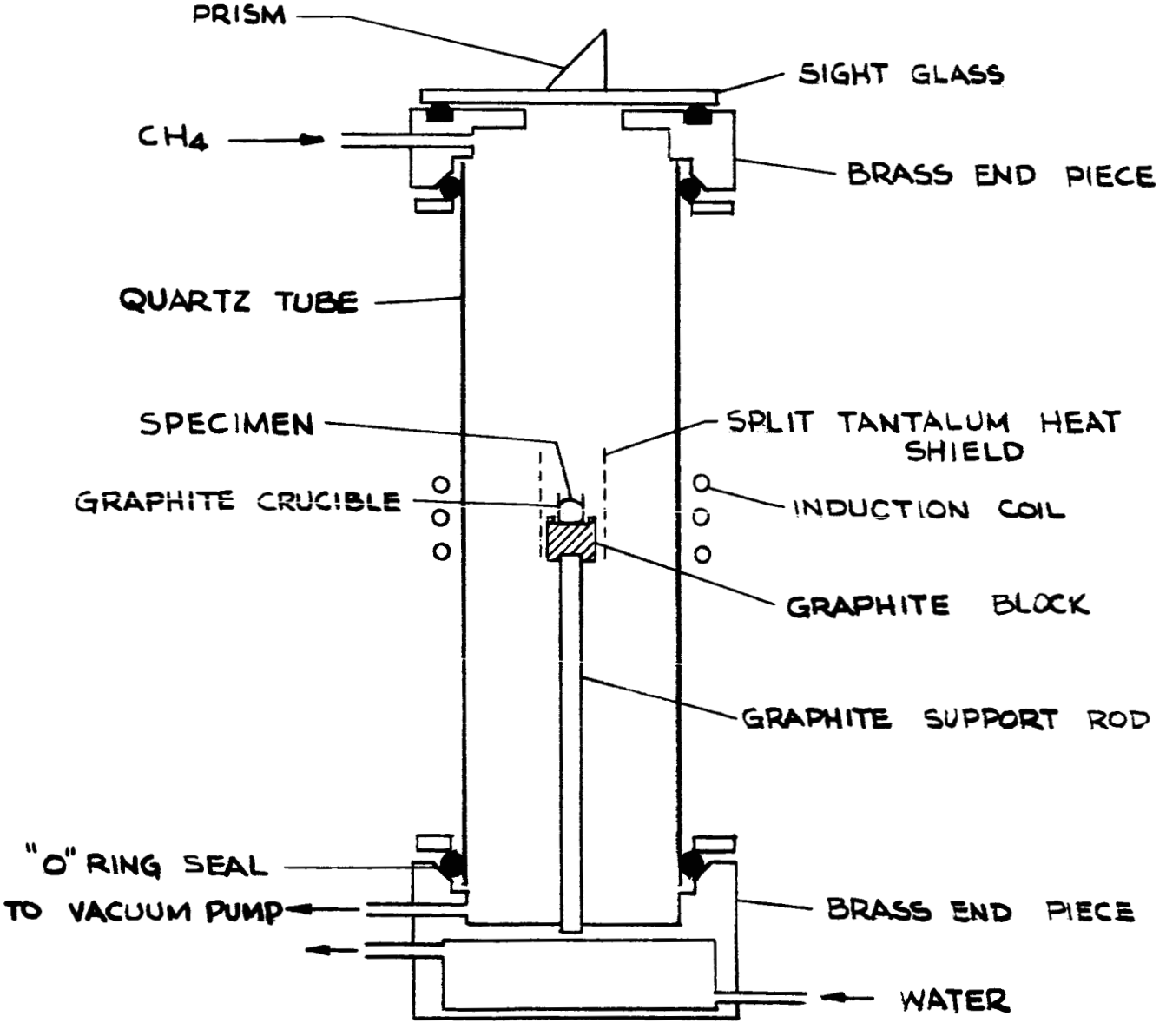
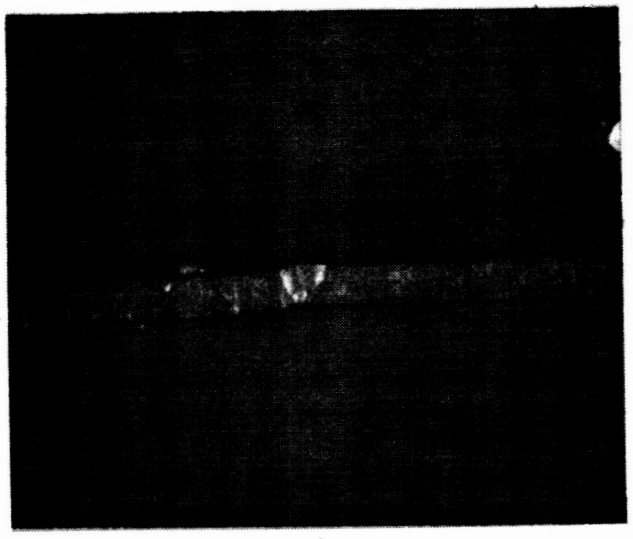
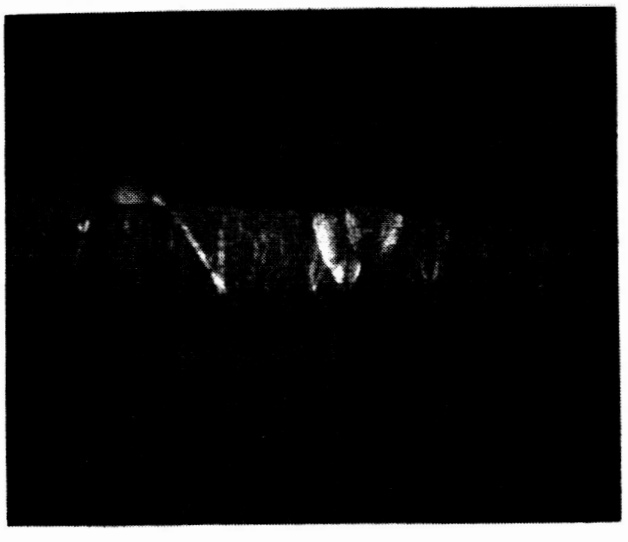


FIG. 5 SCHEMATIC DRAWING OF DEPOSITION UNIT USING INDUCTION HEATING



(X 400)



(X 800)

FIG. 7 TRANSVERSE SECTION THROUGH PYROLYTIC GRAPHITE DEPOSIT VIEWED UNDER POLARIZED LIGHT

TABLE I

TYPICAL RESULTS OF DEPOSITION EXPERIMENT ON LIQUID PLATINUM

Corrected Temperature (°C)	Methane Pressure (MM. Hg.)	Time (mins)
2160	5	0
2245	5	5
2245	5	10
2245	10	15
2245	8	20
2175	9.5	25
2205	9.5	30
2195	9.0	35
2180	9.0	40
2175	9.5	45
2160	10.0	50
2160	10.0	55
2180	10.0	60

APPENDIX

I. INTRODUCTION

In addition to the deposition of pyrolytic graphite on a liquid substrate, some subsidiary experiments were carried out on the possibility of using a solid metal substrate for deposition.

As in the case of the liquid substrate, the essential requirements were a high melting point, low vapor pressure, and a minimum amount of chemical reaction with carbon. A survey of the available literature on carbon-metal alloy systems indicated that the most promising material from the point of view of chemical reactivity appeared to be iridium. This, together with its high melting point (2443°C) and low vapor pressure indicated that iridium might possibly be an ideal material on which to attempt pyrolytic graphite deposition.

II. EXPERIMENTAL PROCEDURE

A strip of iridium 0.005" x 1/4" x 1-5/8" was resistance heated between water cooled electrodes in the vacuum apparatus described in Section II.2. The temperature of the strip was slowly raised to 1800°C by increasing the current. Methane gas was finally admitted at a flow rate of 0.25 lpm and a pressure of 4 mm Hg. In this particular run, the iridium strip burnt out after a reaction time of only one to two minutes. This was possibly due to an exothermic reaction occurring between the deposited carbon and the iridium which may have resulted in localized melting of the strip. It was therefore decided to lower the deposition

temperature in subsequent runs so as to avoid any localized melting.

In the second deposition attempt, the methane was admitted into the apparatus at a flow rate of 0.25 lpm and a slightly higher pressure of 11 mm Hg. An immediate increase of 150°C in the iridium temperature was observed, and the power input was therefore cut back until the temperature remained steady at 1700°C. The reaction was continued for forty-five minutes. The iridium strip was removed from the apparatus and a smooth but uneven deposit was observed on both sides (Fig. 1). A metallographic section was taken through the strip.

III. EXPERIMENTAL RESULTS AND DISCUSSION

The metallographic section taken through the strip clearly revealed pyrolytic graphite deposit on the iridium. A section through the coated strip is shown in Figure 2. In Figure 2 the pyrolytic graphite stripwhich has separated from the iridium strip is clearly visible.

A puzzling feature of the results obtained is the uneveness of the graphite deposit. This is shown clearly in Figure 1 in which apparent depressions in the film surface can be seen. In figures 3a, b, c, high magnification photographs reveal the depressions in more detail. Figure 3a shows an uncoated portion of the iridium strip surrounded by a pyrolytic graphite layer. The dark areas around the uncoated portion are due to a gradual variation in thickness at the edge of the film. Figure 3b is the area adjacent to that shown in Figure 3a, and the surface structure of the pyrolytic graphite is illustrated in this photograph. The right hand edge of this photomicrograph shows one of the depressions in the pyrolytic graphite strip, and is indicative of a pyrolytic deposit of a small thickness than that shown on the left hand side. Figure 3c is the adjacent section of the strip to 3b, and is a more extensive photograph of the thinner of the two deposited layers.

The phenomenon shown in Figure 3 and described above is difficult to account for. However, a possible interpretation can be given in terms of the growth mechanisms of thin films.

If the assumption is made that in the ideal case, on an almost structurally perfect substrate, all growth originates from a single nucleus and gradually the deposit spreads out over the whole of the substrate, the results obtained in the present work may be explained. Once the original layer has started spreading, it is feasible that one or more nucleation sites will occur on its surface. Growth would normally occur at such sites and eventually spread over the whole of the surface. However, in the present experiments, it is possible that due to the low pressure and short deposition time involved, only the graphite layer first nucleated had sufficient time to cover the whole of the substrate surfaces. Subsequent nucleated layers would probably not have had sufficient time to grow over the whole of the surface, therefore leaving what appeared to be apparent depressions in the pyrolytic graphite deposit.

A second important feature of the present results was the effect of the graphite deposition on the iridium strip. Before deposition commenced, the iridium was quite ductile. However, after deposition, although parts of the deposit did break away quite easily from the iridium, the general tendency was for the deposit to adhere to the strip, and in addition the strip was brittle and broke easily. From this point of view, therefore, it appears that iridium will not be a suitable substrate for the continuous deposition of pyrolytic graphite filaments at the high temperatures used in the present work.

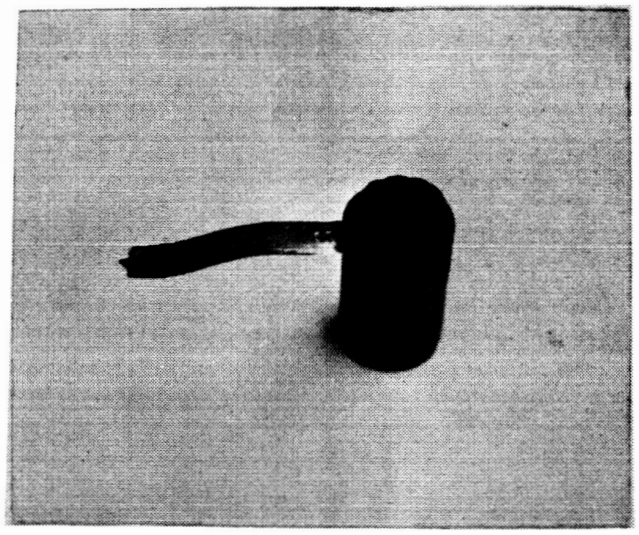
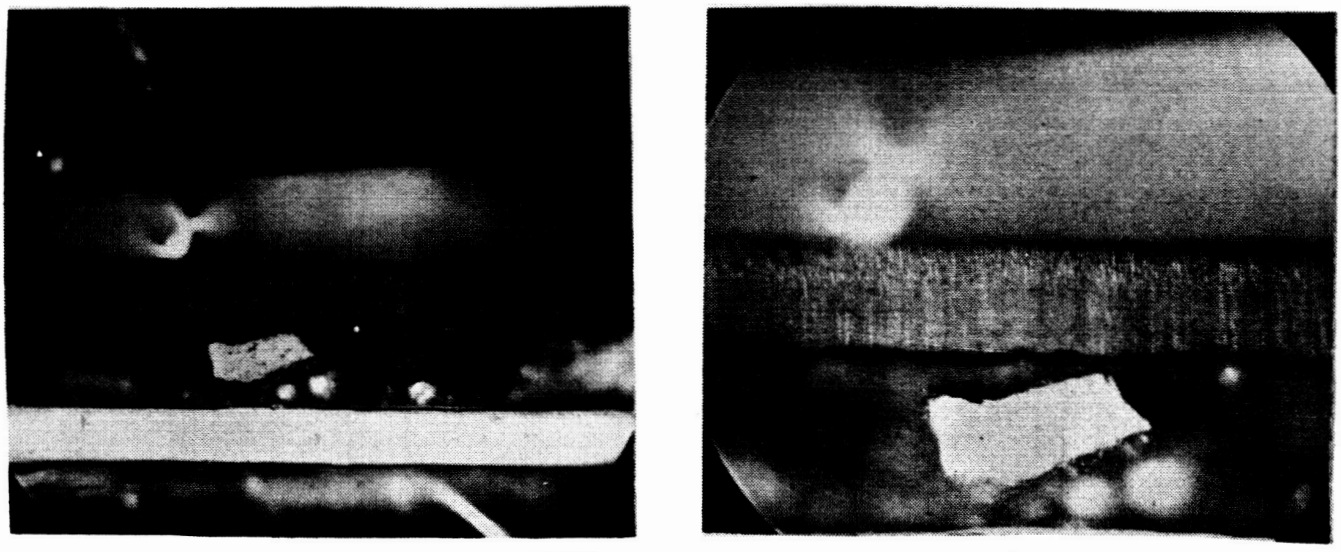


Fig. 1 MACRO PHOTOGRAPH OF PYROLYTIC GRAPHITE DEPOSIT ON IRIDIUM STRIP



(a) (200) (b) (x400)

Fig. 2 - SECTION THROUGH PYROLYTIC GRAPHITE FILM

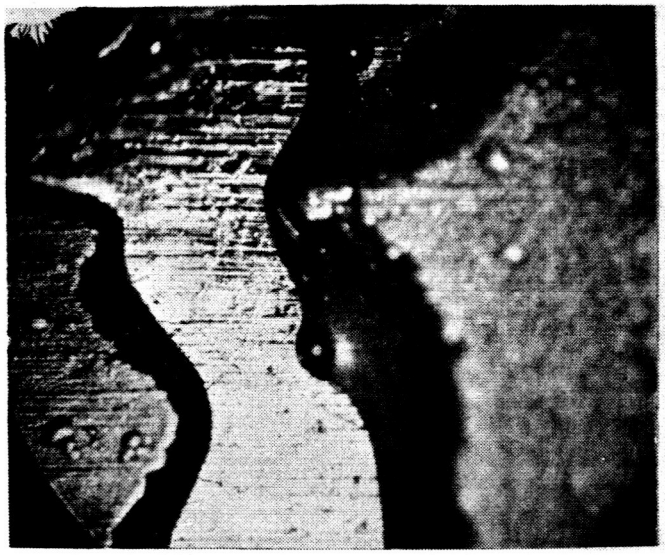


Fig. 3a (x100)

Fig. 3b (x100)

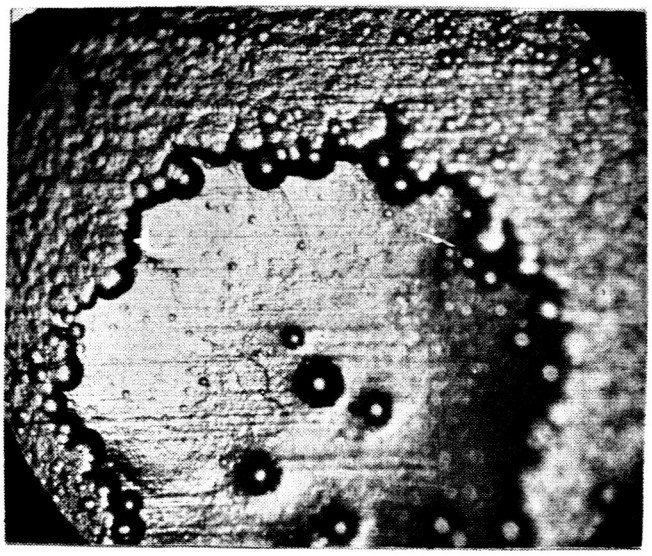


Fig. 3c (x100)

Fig. 3 - PHOTOMICROGRAPH OF ONE OF DEPRESSIONS IN PYROLYTIC GRAPHITE DEPOSIT