(Preparation of Pyrolytic Graphite (PG) Shell Using CVD Technique)

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Abstract

A Pyrolytic graphite (PG) shell was produced by Chemical Vapor Deposition (CVD) using a new modified vacuum furnace. The deposition experiments of (PG) were achieved on a substrate of solid rods and slabs of commercial graphite. This was selected as a miniaturized mandrel for deposition experiments. The substrate was heated at temperature range of (1500ºC-2300ºC) and a hydrocarbon gas (liquid benzene) was used with a pressure range of (1.5mbar- 2.5 mbar).A flow of hydrocarbon gas was admitted into the chamber and the PG was deposited by decomposition of the gas at high temperature on preheated graphite mandrel as previously mentioned. Methane gas was also used for deposition experiments at high temperature range (1700ºC-2000ºC) and pressure range of (100mbar-200mbar) .The thickness of the prepared material was measured as a function of T, P and time. An x-ray diffraction analysis has been done for the prepared PG shell and compared with standard grid electrode for high power electronic tubes made of PG. The calculated density of the deposited layer produced in this work at maximum temperature was about $(2.1\pm0.1 \text{ g/cm}^3)$ .A high temperature calibration was achieved using Stephan -Boltzmann's law for different melting point metals (Cu, Ni, Ta, Mo).In addition an optical pyrometer was also used for this calibration. Finally, the prepared PG shell of this work was exposed to a high temperature oxyacetylene burner test at the atmosphere. The test shows no visual deformation of the external material.

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تحضير قشرة الكرافايت الحراري باستعمال تقنية CVD

الخلاصة

ان تحضير قشرة الكرافايت الحراري بطريقة الترسيب بالبخـــار الكيميـــاوي (CVD) يتطلب منظومة تفريغ مجهزة بحجرة تم تحويرها بشكل فرن فراغـــي . تـــم تحقيـــق تجـــارب الترسيب على قواعد من الكرافايت التجاري بشكل قضيب صلب و شـــرائح . اختيـــرت هـــذه النماذج (القوالب) على هيئة قوالب مصغرة لعملية الترسيب . نسخن القالب لدرجات حـــرارة من (1000°C - 2300°C) ويستعمل الغاز الهيدركاربوني (البنزين السائل) عنـــد ضـــغط يتراوح بين(2.5mbar - 1.5) . يتم ادخال الغاز الى الحجرة . لكي يحصل ترسيب الكرافايت الحراري اثناء عملية تفكك الغاز عند درجات الحرارة العالية . استعمل غـــاز الميثـــان ايـــضا لتجارب الترسيب عند درجـــات حـــرارة (1700°C - 2000°C) و ضـــغط (200mbar - 100) . تم قياس سمك الطبقة المترسبة من الكرافايت الحراري في كلا الحـــالتين (البنـــزين و الميثان) كدالة لدرجة الحرارة و الضغط وزمن الترسيب . اجريت تحاليل حيود الاشعة السينية للنماذج المحضرة وتم مقارنتها بنماذج قياسية تم الحصول عليها مـــن قطـــب شـــبكة الـــصمام الالكتروني ذات القدرة العالية الذي يصنع من مادة الكرافايت الحراري كما هو معروف . تبـــين ان الكثافة المحسوبة للكرافايت المنتج في هذا البحث كانت تساوي حوالي ($2.1\pm0.1 \text{g/cm}^3$) . اعتمدت طريقة تعير درجات الحرارة العالية على معادن ذات درجات انصهار عالية(النحـــاس, النيكل, التانتلوم , الموليبدنيوم) واخيرا تم فحص القشرة المحضرة في هذا البحـــث بتعريـــضها

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لشعلة من الاوكسي استلتين ذات درجة حرارة عالية في الجو الاعتيادي و اثبت عدم ظهور اي
تشوه عياني للطبقة الخارجية.

Introduction

Pyrolytic graphite PG is unique form of graphite with interesting mechanical and electrical characteristics. PG is grown on mandrel by chemical vapor deposition process of hydrocarbon decomposition. This process of chemically reacted volatile compounds of material to be deposited, with other gases, to produce a nonvolatile solid those deposits on suitably substrate [1]. The PG is vapor deposited from carbon which is characterized by strong anisotropic properties [2]. The graphite as deposited by cracking hydrocarbons around (2000°C) shows preferred orientation with consequent anisotropy and proved that a subsequent annealing around (3400°C) produces crystal properties comparable with those of natural single crystals [3]. The evidence of single crystal was shown in highly annealed of PG heat treated at (3600°C) [4].A new studies were also indicated that PG structure becomes similar to that of natural graphite after a heat treatment at (3000°C) [5].Mechanical strength and thermal expansion tests on two micro structural types of PG were carried out from room temperature to (2760°C). Results indicate that PG yield higher, more reliable mechanical property values [6]. For making PG films , it is preferable to use tin as substrate at temperature range (1600°C-1800°C) ,at atmospheric pressure, a source gas consisting of methane and argon , helium or hydrogen [7].The mechanism of PG formation studied at temperatures range (1440°C – 2215°C) and propane gas (5-200 torr). It was found that the various mechanisms of formation are closely related to the microstructure of PG [8].The structure of PG has been examined by x-ray diffraction for several samples deposited under various conditions at (1340°C-2310°C) and (5-200 torr) [9]. The studies of graphite deposited by pyrolytic processes shows that the mean deposition rate is a function of hydrocarbon concentration ,diluents types, gas velocity , temperature and pressure [10].The manufacturing methods for producing PG in various shapes and structures are effected by the process parameters (T,P and gas flow) [11].It has been shown that the deposition processes occurring at various temperatures and pressures using natural , pyrolytic and commercial graphite [12]. Pyrolytic graphite was widely used for high temperature applications .Some of these applications are used for coatings rocket nozzles [13, 14] and also used to fabricate grid structures in some high power electronic tubes due to their high

temperature properties [15, 16, 17, 18, and 19].

In the present work, PG layer were deposited on commercial graphite substrate .This substrate was electrically heated to (1500ºC-2300ºC) in an evacuated chamber to pressure of (10^{-5} torr).The hydrocarbon sources were liquid benzene driven inside the chamber with the aid of the applied vacuum through a dosing valve. Another hydrocarbon gas (methane) was also used for a deposition experiments.

Apparatus and experimental procedure:

The apparatus in the present work consists of a stainless steel vacuum chamber with water cooled jacket and two main high voltage water cooled electrical feedthrough. Both systems were cooled by main chiller (5-10ºC). The graphite mandrel (rod) to be used was fixed inside the chamber between the two electrodes and can be heated by the passage of high electric current (D.C) with low voltages. The vacuum system is consisting of rotary and diffusion pumps and can achieve pressure around

(10^{-5}torr).The pressure inside the chamber are measured using a pirani and penning gauges. The temperature was calculated using Stefan-Boltzmann's law as mentioned in the next high temperature calibration section. The apparatus used is illustrated in figure (1).

The commercial graphite mandrel (6mm diameter and 60mm solid rod) was accurately measured using enlarger system with (20x and 40x) and fixed

inside the chamber onto the electrodes. The chamber is then evacuated to the desired pressure. The mandrel was heated to the maximum temperature which is higher than the experimental temperature for two minutes and then reduced to the desire value. This was heated at constant temperature for about 15 minutes. When the temperature is steady, a gas inlet (liquid benzene with purity of 99. 99% or methane) through a variable needle valve was admitted at a constant desired pressure. Thick deposited layer as a function of time was obtained. A continuous deposition was developed to produce thicker layer.

High temperature calibration:
High temperature measurement is a crucial parameter for the CVD experiments of PG preparation. As a results of the sensors measurements limitations for high temperature range (1600°C-2200°C) inside vacuum furnace. The purpose of this section is to find a common reliable temperature measurement procedure .One of the suggested method in this work was the optical pyrometer technique. This method was not applicable because of the IR (from optical pyrometer) absorption occurred due to the presence of the hydrocarbon gases inside the experimental chamber.

So, the alternative method which overcomes this problem was to do an experimental calculation with standard metals of known melting points.

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According to Stefan-Boltzmann's law, the energy emitted by a black body per unit area and unit time is proportional to the power four of the absolute temperature of the body .This law is also valid for so called grey body whose surfaces shows emissivities less than one and approximately equal to one for black body using the relation :

$$P = IV = \text{Є} \, \sigma \, A_s \, T^4 \qquad \dots (1)$$

Where Є is the emissivity ($\leq$ 1), σ is Stefan's constant = 5.67×10^{-8}(Watt / m^2.K^4), A_s is the sample surface area and T is the temperature. Experimental calculation procedure was started as follows:

Firstly; calculations have been done to insure the satisfaction of the relation (1) using high temperature melting point metals (Ta, Mo, Ni, and Cu) as previously mentioned. The power was applied to heat the metals individually and measured the current and voltage up to the breakdown voltage (melting). Calculated (T_c) and standard (T_s) melting temperatures are shown in Table (1) .These results were successfully confirmed using equation (1).

Secondly; a graphite solid rod was fixed and heated inside the chamber within temperature (1500°C-2300°C) in the absence of the hydrocarbon gases. The input power was also measured across the graphite and (Tc) was calculated using equation (1).In the same time an optical pyrometer was fixed across the chamber to measure the temperature (Tp) .The complete results is shown in Table (2). The power density as a function of the calculated temperature (T_c) fitting curve was plotted as shown in Fig (2). This results a calibration formula:

$$T(°C) = 5.348P(W) + 1224.76 \qquad \dots (2)$$

This formula was used to obtain the temperature during the (CVD) experiments in this work.

Experimental results and discussion:

Many experiments were performed to produce PG using high temperature and pressure CVD method. The material was grown onto a mandrel of commercial graphite solid rod. A first set of deposition experiments for different parameters like temperature, pressure, time, and deposition thickness using (benzene) have been done as listed in Table (3).A second set of experiment was also produced using benzene at a constant pressure, variable temperature and time are listed in Table (4).Data in Table (4) are shown in figure (3) and (4) .Figure (3) shows the deposition thickness as a function of time for high temperature rang (2000ºC-2300ºC) at constant pressure (1.5mbar) .These results a deposition rate varying from (1.5µm/min. to 2.0µm/min). Figure (4) shows the deposition thickness as a function of temperature at pressure. A third set of experimental data can be seen in Table (6) using methane gas at high constant temperature (1700ºC).A fourth set of experimental data was obtained, listed in Table (6) and shown in

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figure (5) .This shows the deposited thickness as a function of different temperatures .The result shows a deposition rate range (1.5µm/min_3.0µm/min) for a wide range of temperatures. The best result was observed at high pressure (150mbar), high temperature (2000ºC) at period of (60min.). Obviously, the deposition yield for methane gas was higher in comparison with benzene.

A specimen was selected from the grid of the high power electron tube (Thomson) [18] and an x-ray diffraction analysis has been taken as standard results for PG. This analysis was concentrated on comparison of the results of the standard sample of PG and the results obtained from this work. The analysis is compared in figure (6).This analysis shows the similarity between the two results obtained from two different sources. This indicates that there is a confirmation of PG prepared in this work. Finally, a photograph of figure (7) shows the mandrel and the PG shell in real size obtained by CVD method.

A visual observation of the prepared PG shell shows a shinny, silvery in color almost smooth and hard surface with calculated density $(2.1\pm0.1g/cm^3)$.So it was discovered that a reasonable uniformly distributed along the substrate at low deposition rate (1.5µm/min.) can be obtained.

Conclusions

The deposition of pyrolytic graphite at high temperatures could be successfully achieved with a vacuum furnace. A deposition with two different hydrocarbons was used and the result shows small differences in the deposition parameters. The layers with large and small thicknesses could be obtained and can be easily separated from the substrate. The PG deposited thickness using benzene with low pressure was higher than that for methane at high pressure. An average deposition rate (2.5 µm / min) can be obtained for both benzene and methane. Maximum thickness of PG shell was about (500µm) with density of about (2.0 g/cm^3).This hard shell proved to resist a high temperature condition.

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Table (1) High temperature calibration data for metals.

Expt. No.	Metal	Tc(C°) M.P(calculated)	Ts(C°) M.P. (STD)
1	Cu	1087	1083
2	Ni	1455	1454
3	Mo	2609	2607
4	Ta	2979	2977

Table (2) Temperature calibration data using optical pyrometer.

I (amp.)	V (volt)	P (w/ Cm^2)	Tp (° C) / pyrometer	Tc (°C) / calculated
280	5.3	71.62	1585	1598
300	5.51	79.77	1640	1650
320	5.92	91.42	1710	1718
340	6.51	106.82	1790	1796
360	7.1	123.32	1877	1874
380	7.8	143.05	2003	2017
400	8	154.44	2050	2060
420	8.72	176.75	2130	2140

Table (3) Results of PG deposition experiments using BENZENE.

Expt. No.	Press. (mbar)	Temp (ºC)	Time (min.)	Thickness (mm)
10	1.5	1837	80	70
20	1.5	1870	65	55
30	2.5	1750	60	285
40	2.5	1650	105	195
50	2.5	1560	68	55
60	2.5	2010	55	500

**Table (4) Results of PG deposition experiments at (p=1.5mbar)
using NENZENE.**

Expt. No.	Time (min.)	T(ºC)	Thickness(µm)
25	50	2056	82
26	50	2376	108
27	150	2066	255
28	150	2238	300
29	210	2218	500

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**Table (5) Results of PG deposition experiments
at T= 1700ºC using   METHANE.**

Expt. No.	Thickness (mm)	Time (min.)
70	4	30
71	120	25
72	120	25
73	100	80
74	260	120
75	125	60
76	330	120
77	100	60
78	280	90
79	340	120
80	175	60
81	260	120

.   **Table (6): Results of PG deposition experiments at (60min.)
using METHANE**

P (mbar)	Thickness (µm)		
	T = 1700º C	T = 1800 ºC	T = 2000º C
100	125	150	150
150	100	170	200
200	175	100	100
200	-----	150	150
260	-----	100	100

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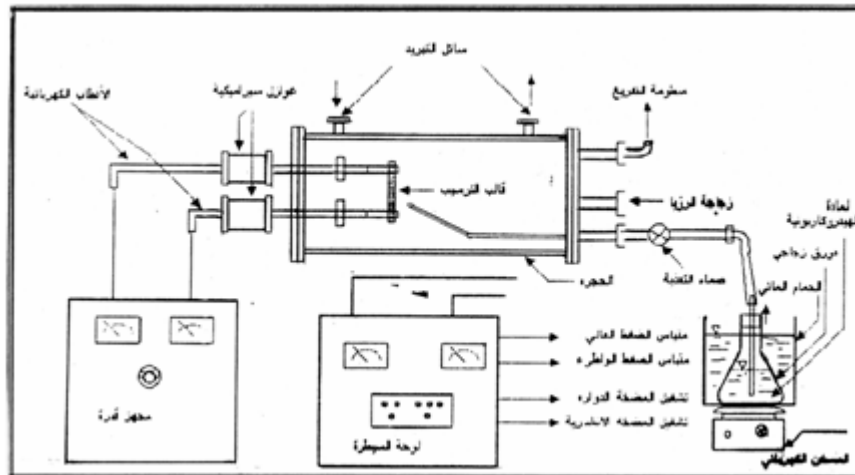
Figure (1) Schematic diagram of vacuum furnace chamber

$$y = 0.1871x - 229.03$$
$$R^2 = 0.9931$$
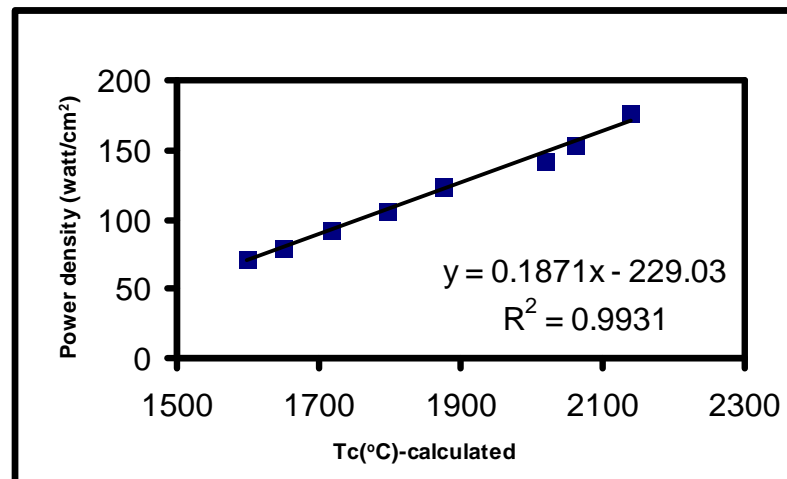
**Figure (2) Shows fitting curve for the calculated
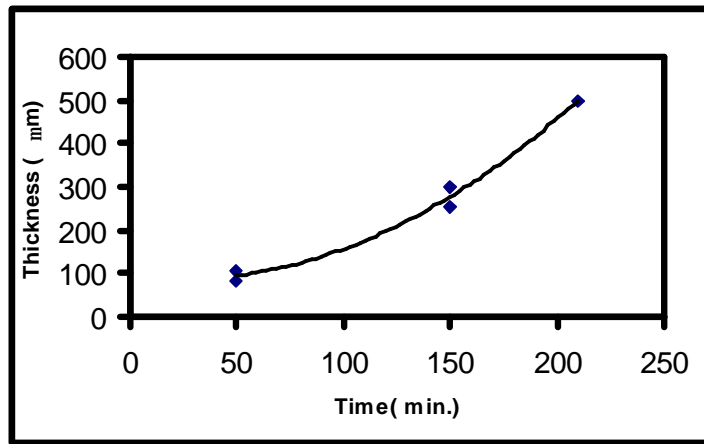(T_c) temperature versus power density**

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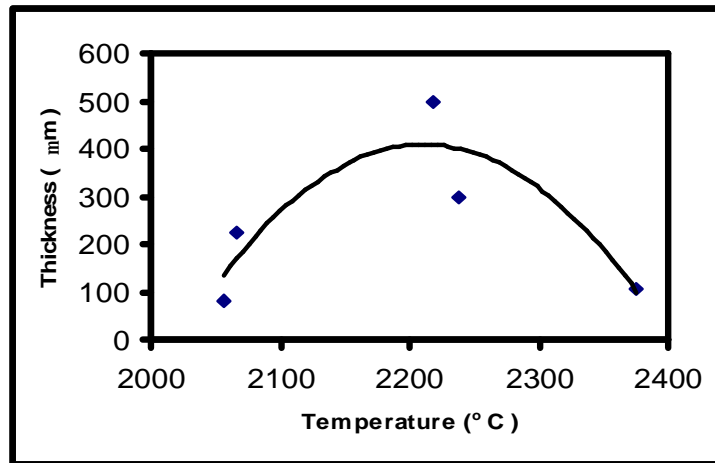**Figure (3) Shows deposition thickness versus time at P= 1.5 mbar for BENZENE.**

Figure (4) Shows deposition thickness versus temperature at P = 1.5 mbar using BENZENE.
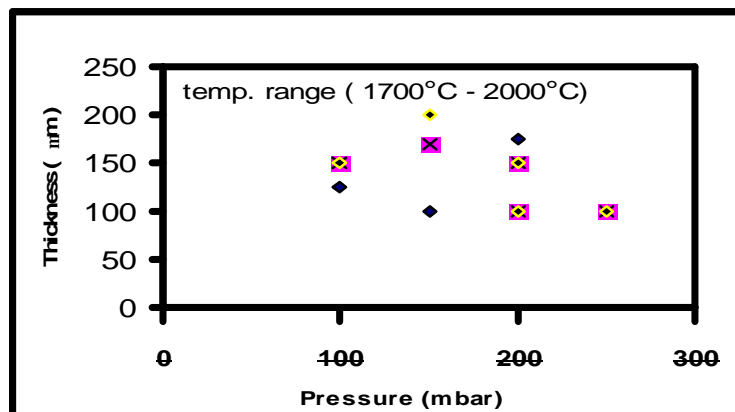

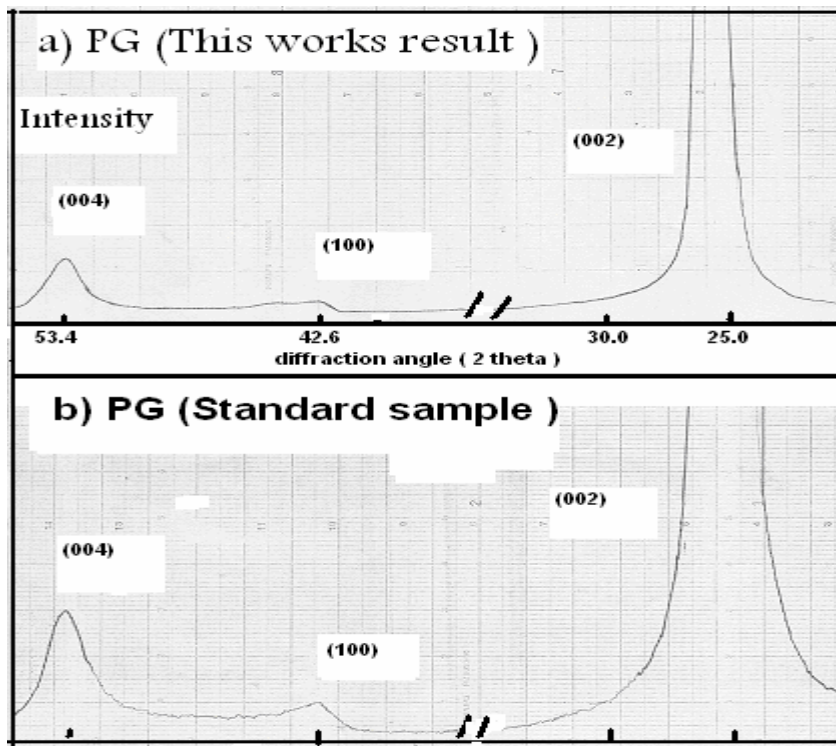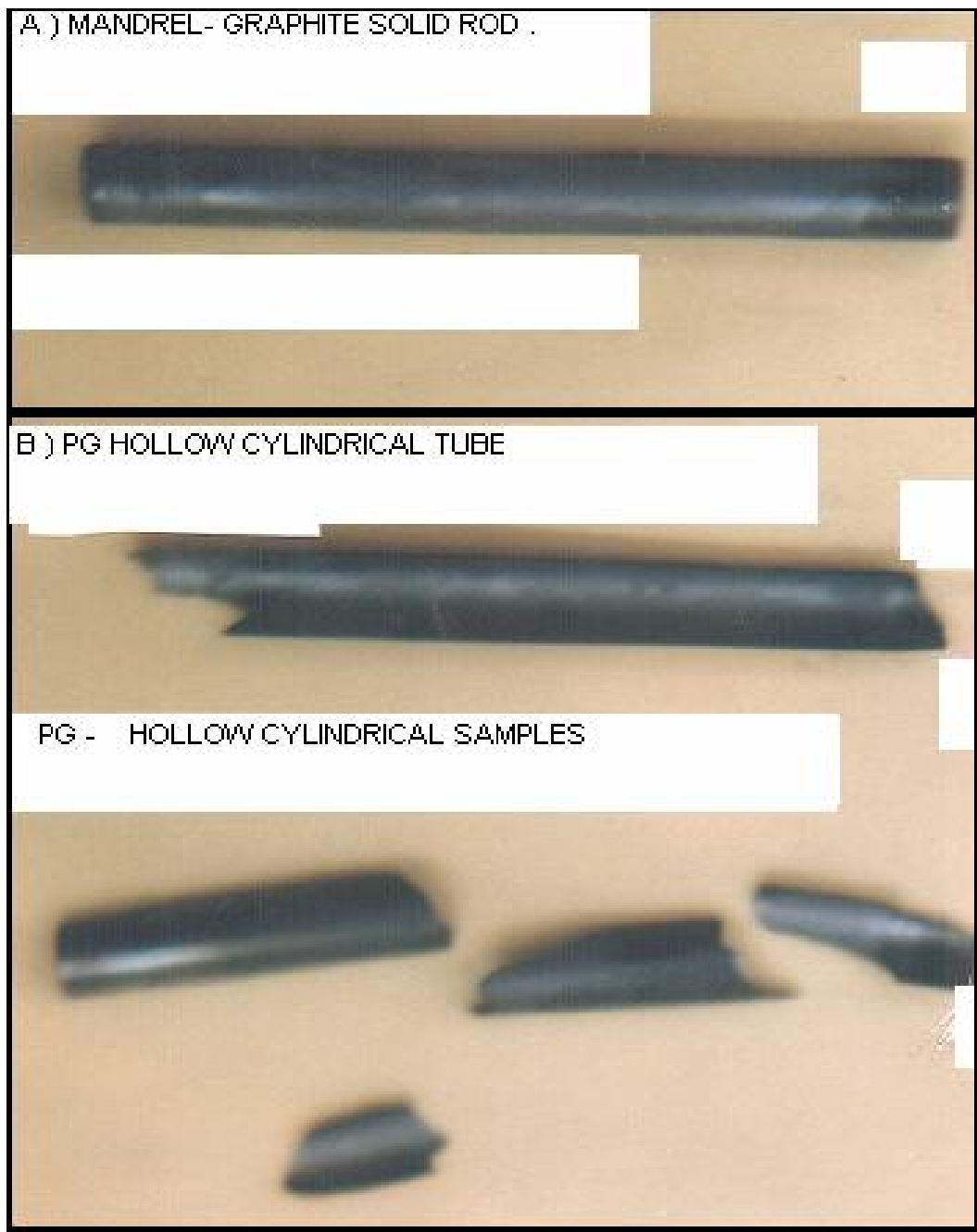**Figure (5) Shows deposition thickness versus pressure for METHANE**.

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Figure (6) Shows (XRD) comparison

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Figure (7) : Shows a photograph (1:1);
a) Substrate mandrel   of commercial graphite solid rod ;
b) Prepared PG shell = 500µm thick .