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JOURNAL OF UNIVERSITY OF BABYLON

For ENGINEERING SCIENCES (JUBES)

Vol.30, No.3.| 2022

The Principles of Production and Applications of Pyrolytic Carbon as Biomaterials-Review

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Received:	14/8/2022	Accepted:	21/9/2022	Published:	22/9/2022

Abstract

The growth in modernistic surgery is especially related to expansion of biomaterials. The interior fracture fixation devices, articular prostheses, vascular prostheses, and replace heart valves are models in this part. A great attention to the carbonaceous materials due to the strong potential biocompatibility, wear resistance ,good mechanical properties thus they are used for biomedical applications. All these properties available in pyrolytic carbon. It is a manmade material of carbon and not found in nature. It can be produced by chemical vapour deposition method for biomedical applications. Mechanical heart valves, orthopedic applications as hand and wrist implant made from pyrolytic carbon. This research is described method of production,properties, biomedical applications of pyrolytic carbon.

Keywards: Pyrolytic carbon, Chemical Vapour DepositionCVD, Pyrolysis, Biomaterials

1.Introduction:

The biomaterials are a special type of matters that are distinguished by diverse composition, framework, and selected biological, chemical and mechanical feature. These materials should have biocompatibility with living tissue to be biomaterials. That mean does not induce body immunoreactions or interfere and or disturb surrounding organ system [1].

The biomaterials should be biocompatible, resist corrosion, compatible with bone ingrowth, enough mechanical properties, enough young's modulus and fatigue strength, availability and process ability. These requirements are achieved by diverse customary sets of biomaterials which lead to showing various behavior depending on functional requirements [2].

There are three classification of biomaterials, often depending on their human body functionality and materials properties. First type relying on member and regulation grade of the epidermal body. The model of this type is the skeletal system can be repaired and restored with a joint replacement and bone plate. At the member level the human heart can be restored and substituted by a synthetic heart valve, overall valve, pacemaker [3]. Second, biomaterials can be classified according to soma, the soma part treated as a synthetic rump joint and kidney dialysis can be utilized to substitute destroyed or sick soma section, whilst screws, sutures, and bone plates can assist in wound healing. Third classification is based on the materials properties as bioceramic,biopolymer and metallic [4].

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The employment of metallic materials for medical implants can be planned boack to nineteenth century. In spite of large numbers of metals and alloys but a few are biocompatible and eligible for long term implants [5].

Carbon is a typical example of bioinert ceramic. The term bio inert indicates to any material has minimal interaction with its surroundings tissue once placed in human body [6]. In the history of man, carbon is the recognized material. Through centuries it is used as a black material for paintings, camouflage and optics [7]. Carbon can occur in many of allotropic styles involving diamond,graphite,graphene, fullerenes, and carbon nanotubes and pyrolytic carbon [8].

A specific shape of carbon element is pyrolytic carbon. It has very suitable for biomedical implementations such as mechanical heart valves, joint replacement, hand as well as wrist applications. The trademark of pyrolytic carbon is pyrocarbon [9, 10, 11] .

2-History of Pyrolytic Carbon:

In 1950 and 1960, an artificial material is developed as pyrolytic carbon in nuclear manufacturing [12]. The effective biomaterial of pyroletic carbon was advanced at General Atomic through the late 1960 by used a fluidized-bed reactor [13, 14].

In the main nomenclature, it was treated as low temperature isotropic carbon(LTI carbon). The former impersonal mechanical valve as clinical implant of pyrolytic carbon component in the DeBakey-Surgitool in 1968 [13].

Because of its tribological characteristics strength-to-weight ratio, unique directional thermal properties and biocompatibility especially with blood, led to expanding of its applications to the medical field for mechanical heart valves, with and without silicon in 1969 [12, 15]. Pyrolytic carbon used in 1969 in mechanical heart valve component. The implantation of mechanical heart valve completely from pyrolytic carbon in 1977 [16] .

Dr. Bokros and his team extend a pure carbon implant onto market in 1996. They produced pure pyrolytic carbon which is tougher and stronger than pyrolytic carbon alloyed with silicon. Pure pyrolytic carbon is more biocompatible and it doesn't include silicon carbide inclusions.They can compromise the thromboresistance of the carbon [13].

The prospect of Pyrolytic carbon as a substance for orthopaedic implementations was known and examined. In baboons the preclinical seeking contained groups of pyrolytic carbon metacarpophalangeal (MCP) finger joint implants. After that MCP replacements were cultivated in patients between 1979 and 1987. The prime performance of pyrolytic carbon in small joint of orthopedic devices was proven.[15, 17]

3-Literature Survey:

This section will shed light on the most impoetant related works conducted in this area of interest:

In 1982, Schoen and others looked for the abrasive wear of seven types of mechanical valves containing pyrolytic carbon components. They were implanted for 50 months. All of them

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had not discrenable wear. They suggested clinically considerable abrasive wear did not be a late complexity of cardiac valve surrogate with pyrolytic carbon prostheses [18].

In 1985, Thomas and others studied the impact of various superficial processing on the retention distinctive of the implant. Five kinds of surfaces were studied deposited, smooth grit-blasted,rough grit-blasted, ground, and plasma oxygenated. They were estimated in vivo by situation transcortically in the femora of extreme metis dogs for 12 to 24 weeks. The greatest interface streng was obtained from the deposited implants at 12 weeks. After 24 weeks implantation, the outcomes of mechanical test marked no statistically considerable variation among the interface strength rates or among the interface stiffness rates of the implant. The ability to duplicate the bilogical response to the as-deposited low temperature isotrobic pyrolytic cappears arbon surface appears bossibby one or more of the tratment evaluated [19].

In 1995,Goodman S. and others studied the surface morphology of three types of low temperature isotropic pyrolytic carbon (LTIC) valve leaflet were produced from three different companies. Low voltage scanning electron microscope reveals that LTIC leaflets have a complex topography of 10 nm to 1µm charectrstics with height differences of 100-500nm taking place over lateral distancesof 10-50nm.They obsereved very extensive adhesion and spreading. The extent of platelets interaction on LTIC vascular prosthetics may have been previously underestimated [20].

In 1995, Ritchie and others studied pyrolytic carbon as coating on graphite substrate and monolithic material depending on the shatter, fatigue, and indentation properties. Pyrolytic carbon had low damage tolerence with fracture toughness between 1 and 3 MPa.$m^{0.5}$ and sensitivity to subcritical crack expansion by both cyclic fatigue and static fatigue. The uncommon charecterstics of indentation in pyrolytic carbon are explained relying on microhardness indentation and scanning probe microscopy [21].

In 1996, Gilpin and others evaluated the stresses which caused failure at contact region between leaflets and orifices in heart valves of pyrolytic carbon. Most of heart valves were pyrolytic carbon deposited on graphite not momolithic of pyrolytic carbon. Touch loads on the layered structures gave rise to initial cracking in the pyrolytic carbon at the interface between pyrolytic carbon and graphite rather than Hertzain surface cracks.When compression stress in the graphite compassed to (414-484) MPa and the tensile stress in pyrolytic carbon accomplished to (207-276)MPa the, the initial cracks occurred at the interface between them. The initial cracks did not scatter as soon as to the surface since they passed into a high triaxial compression stress field [22].

In 2007, Pierre-Yves et al. analyzed the roughness and the interaction of flat free energy of different pyrolytic carbon heart valves with three bacterial types on bio films with scanning electron microscope. The results were explained the adherence of Staphylocoous epidermidis and Pseudomonas aeruginosa dependent on free energy and roughness of pyrolytic carbon. The adhesion with Staphylococcus aureus was independent on free energy and roughness of pyrolytic carbon. The developments of properties of pyrolytic carbon could be reduced the valvular prosthetic infections [23].

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In 2010, Vivek Bajpai and Ramesh K. Singh researched at making the industrialization knowledge base to produce engineered surfaces in pyrolytic carbon –bio plants. They investigated the effect of micromachining method parameters. These parameters were rake angle,depth of cut,tool width, and cutting speed on the response variables. Their trials were managed in the AB plane (parallel to layers) and the C plane normal to the layer to observe the influence of anisotropy in pyrolytic carbon. They noted cutting/thrust forces, surface roughness, chip morphology, and surface morphology. The mean cutting and thrust forces enlarged by 118% and 88% respectively. The surface roughness added to multifold when the cutting plane was varied from AB to C [15].

In 2011, Zhang Jian Hui and others searched on microstructural information of silicon alloyed pyrolytic carbon coating which used for heart valves. Two phases for coatings were pyrolytic carbon and β silicon carbide with crystallite sizes were tiny. The coatings are comprised of spherical particles with diameter (300-1000)nm. There were occationally pores between the spherical particles were welded by laminar carbon. The content of silicon was moderate and scattered uniformly in the coatings [24].

In 2014, Ross M., and J. Klawitterdetermined the wear of pyrolytic carbon depended on abrasive mechanism and explained wear resistance due to Brinell hardness and young modulus. The greater wear resistance with greater amount of stored energy. They observed the wear of pyrolytic carbon for mechanical heart valve was the lowest by comparing to cobalt chromium alloy, titanium alloy and polymeric materials [10].

In 2021, Serino Gianpaolo et al. employed two deposition methods of pyrolytic carbon on mechanical heart valv MHV by multiscale approach of mechanical properties. The crystallite orientation of pyrolytic carbon, was produced at 1300℃, is completely random creating random structure characterized by a chaoatic microstructure.A slow rate of deposition fixed during the first hour of deposition made possible layers of high grade of homogeneity . the identation site and the deposition process affect on mechanical properties and microscale length. Setting the alterations of the deposition process allowing achieving pyrolytic carbon describing by more uniform microstructure ,giving bulk material conceited mechanical properties [16].

4-Structure of Pyrolytic Carbon:

Depending on state of deposition such as type, temperature, concentration and flow rate of the source gas, and the face area of the implicit substrate the type of pyrolytic carbon differs. Many micro structures of pyrolytic carbon as isotropic ,lamellar ,substrate –nucleated with a varied content of hydrogen [11].

Figure (1) represents the difference in structure among diamond , graphite, and pyrolytic carbon as turbostartic. Turbostartic pyrolytic carbon is a graphene that has arrangement within the graphene sheet layers but disorder between the layers with a spacing between the planes taller (about $0.1°A$)than in graphite. The disorder between the layers greatly strenghthen the pyrolytic carbon in comparsion to graphite [10,25].

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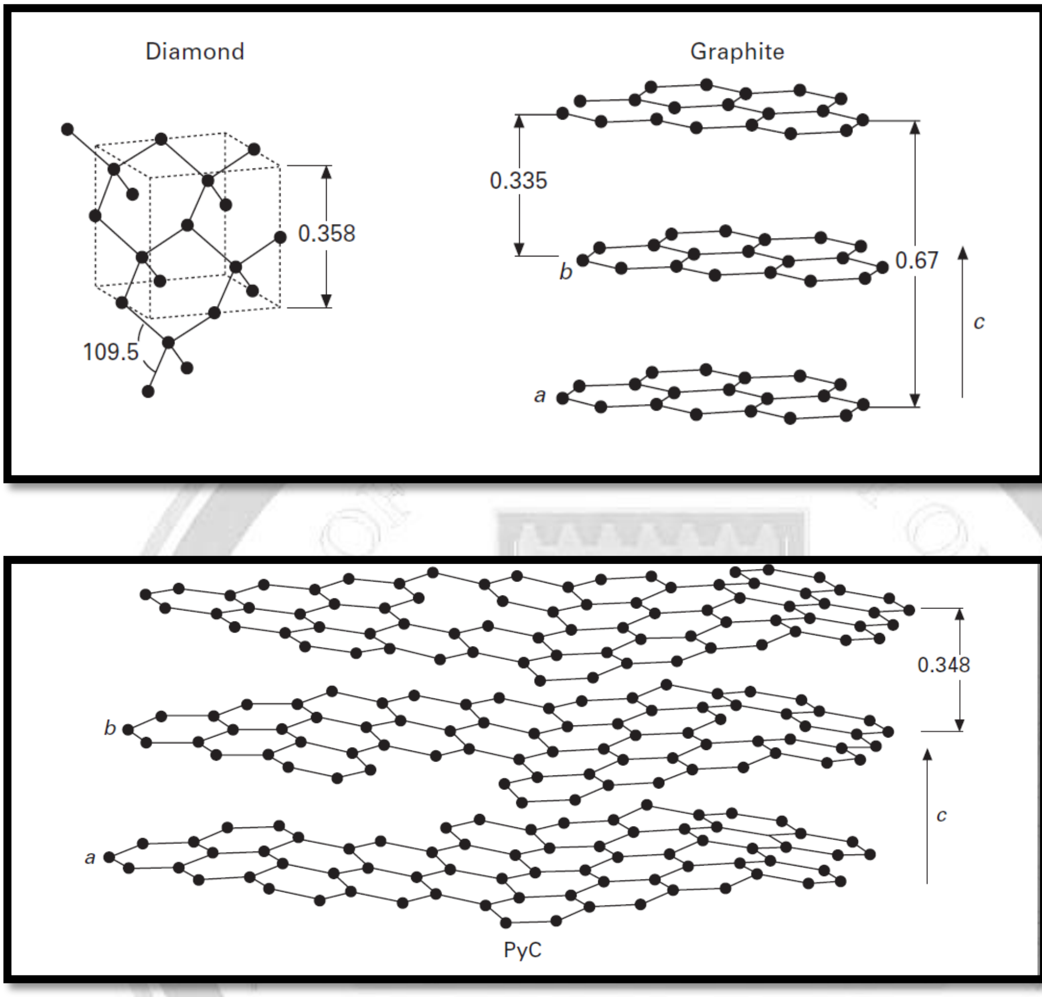

Figure (1): Structure of diamond,graphite, and pyrolytic carbon [10]

4-Method of Production :

Pyrolytic carbon can be produced by methods of deposition as chemical vapour deposition methods and pyrolysis process [12]. The first method of coating heart valve by pyrolytic carbon is the steady state fluidized bed carbon as chemical vapour deposition method. Pyrplytic carbon for mechanical heart valve is highly isotropic and its microstructure contains ultra-fine grains [16]. Silicon alloyed pyrolytic carbon is an exteremely hard and almost perfect linear elastic material with a strain to failure of nearly 1.2 percent [14].

Pyrolytic carbon coating technology and methods of process control were again examined and designed to create pure pyrolytic carbon. The pure pyrolytic carbon has enough hardness and wear resistance. It has higher strength and toughness with higher deformability than the silicon –alloyed material. The elimination of silicon and improvement of mechanical properties had been owned by new pyrolytic carbon. The improvement of mechanical properties

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led to make valve design with greater hydrodynamic efficiency, cancel the need of stiffening rings, thus improving the flow of behavior in the small aortic valve sizes [14].

4-1Chemical Vapour Deposition(CVD):

It is considered the favourable method to produce pyrolytic carbon from a gaseous hydrocarbon. In the beginning the hydrocarbon is inserted to a reactor. Chemical reactions occure above or in nearness the elevated temperature surface of the substrate to create solid carbon. The thermochemical stability of the precursor used affect on the threshold temperature for the carbon deposition. For example the deposition temperatures when using benzene and methane are 600℃ and 1000℃ respectively.The deposition temperature and deposition rate effect the atomic arrangement of the CVD carbon. At high temperature as 2200℃ and low pressure as 10 Torr the anisotropic material pyrolytic carbon is grown. For lower deposition temperatures and /or high deposition rate the disorder increases and preffered orientation lowered. Eventually,amorphous carbon is created at depressed temperatures and elevated deposition rates [25, 12].

4-2 Pyrolysis:

Pyrolysis can be defined as the thermal decopmposition of hydrocarbons in the obscurity of oxygen. Hydrocarbons such as methane, acetylene, propylene, and propane. The decomposition of hydrocarbons without oxygen to carbon dioxide and water cannot happen, in place of a more complicated cascade of decay products occurs that ultimately conclusions in a "polymerization" of the single carbon atoms into major macroatomic arrangements [13].

4-2-1 Applications of Pyrolysis:

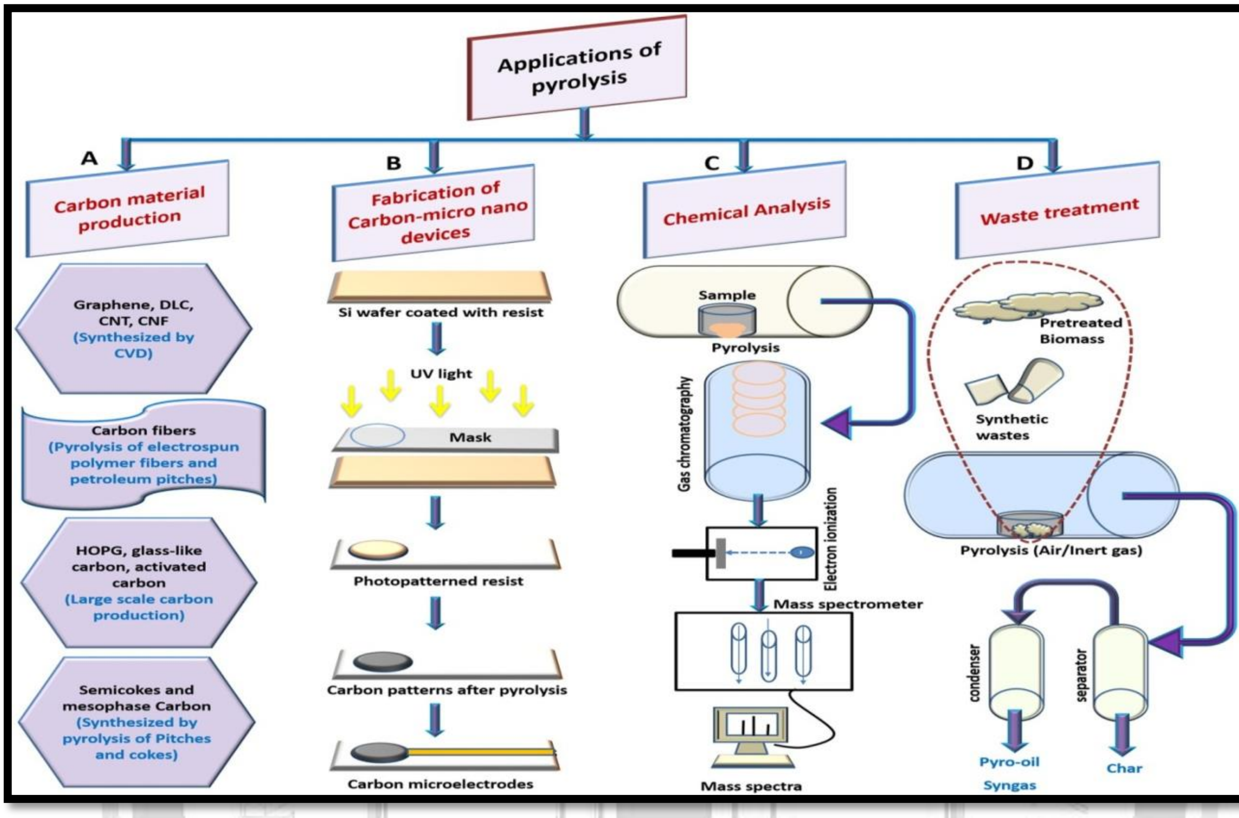
There are four main application areas as shown in Figure(2) :

1. Manufacture of carbon materials.

2. Invention of pre-patterned micro and nano carbon –founded structure.

3. Crash of complicated organic molecules for critical objectives.

4.Waste processing. [26, 27]



Figure(2): Applications of pyrolysis method [27]

4-2-2 Classification of Pyrolysis:

Pyrolysis method can been divided into three groups . First of all depending on the phase of precursor. Second group depending on the scale of reaction and reactor type. Third group is depending on the target product as in Figure(3) [27].

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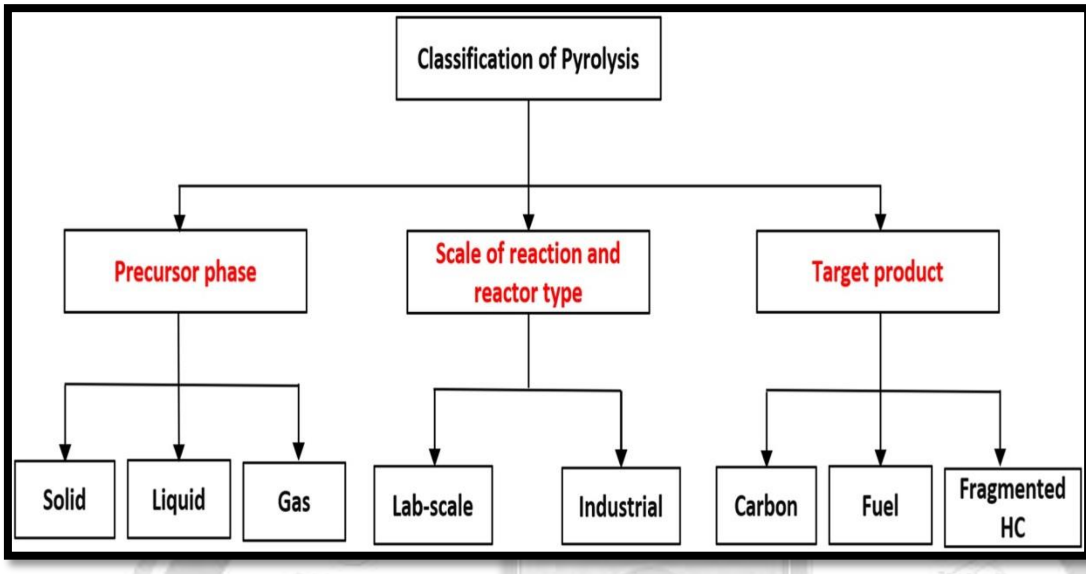

Figure (3): classification of pyrolysis method [27]

4-2-3 Pyrolysis for Pyrolytic Carbon:

Pyrolytic carbon is made ready by elevating the temperature of a hydrocarbon like propane to nearly (1200-1400)℃ without oxygen. After break down the hydrocarbon to free radical of carbon at elevated temperature, these radicals covalently bond to compose the solid pyrolytic carbon. To produce isotropic pyrolytic carbon the fluidised bed reactor is needed as shown in Figure (4). A vertical tube and induction coils can be formed the reactor. The refractory material particles with fine dispersion are put in vertical tube. An inert gas like nitrogen or helium fed in the bottom of the tube where these particles are levitated. The induction coils are responsible of heating the tube [17]. The diameter of reacter ranging from 2cm to 25cm,the best diameter for medical devices is 10cm [13]. If the substrate of graphite is added to the mixture the pyrolysis reaction will take place as in Figure (5).

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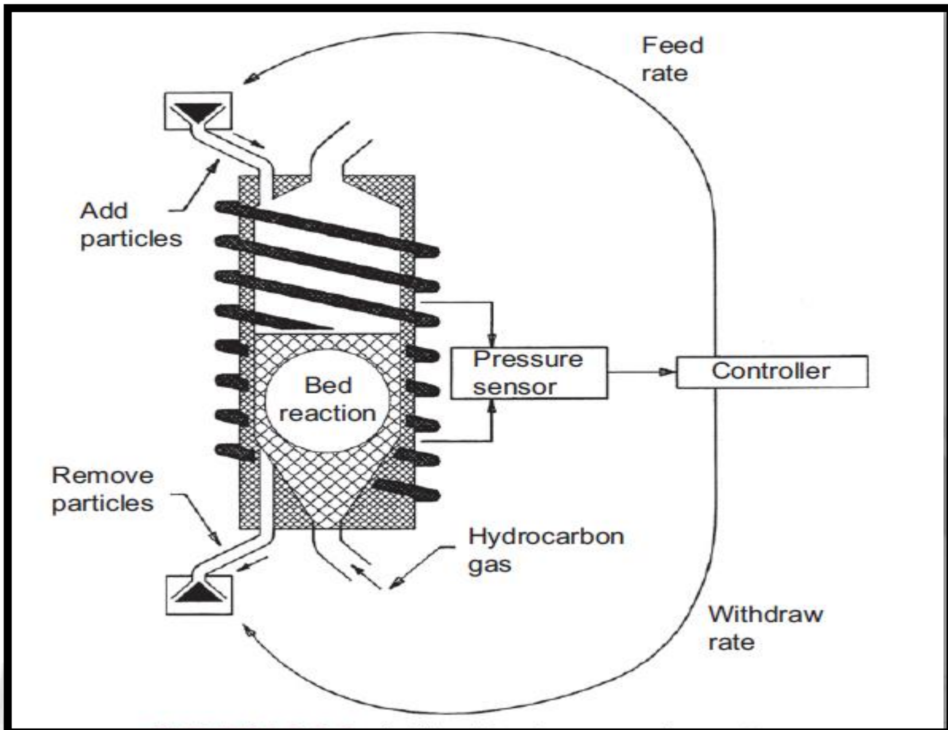

Figure(4): Fluidized –bed reactor schematic [13]

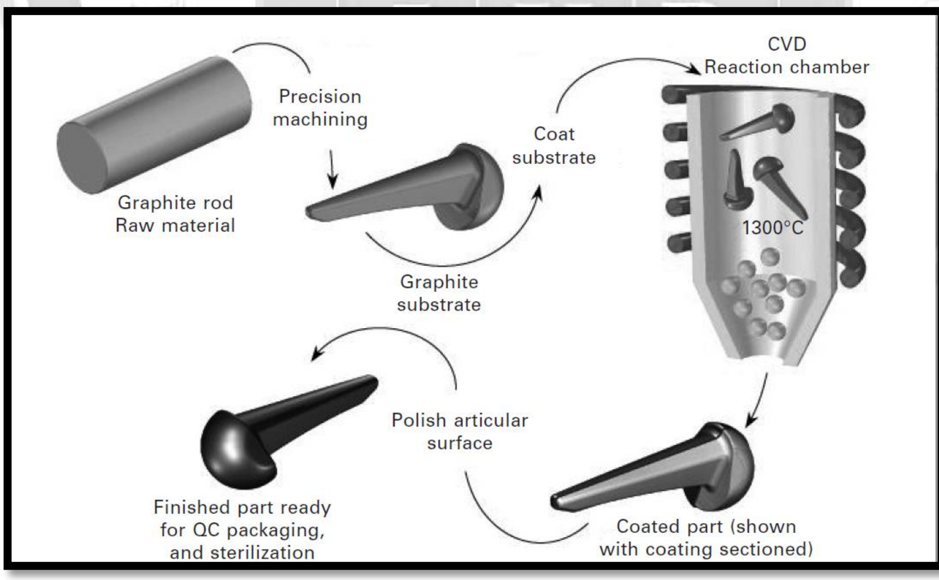

Figure (5): Steps of production pyrolytic carbon coating on graphite [17]

5- Properties of Pyrolytic Carbon:

Biocompatibility,durability,chemical and wear resistance and robustness make pyrolytic carbon attractive for bio and medical applications [27,8]. Blood clots do not readily form on pyrolytic carbon thus it reduces the risk of thromosis [3].It has good electrical conductivity. [27]

Pyrolytic carbon exhibits no appreciable plastic deformation , hard ,rigid linear-elastic material. It has shatter in the value of its tensile strength as most brittle materials. The magnitude of Young modulus approaches that of cortical bone(~17Gpa). Depending on this property the interfacial stress concentrations can contribute to implant loosening and bone reabsorption are minimized [28].The pyrolytic carbon produced from CVD has individual characterstics including mechanical strength and heat conduction [25] .

For biomedical applications pyrolytic carbon can be deposited on very few materials because the coefficient of thermal expansion. Coefficient of thermal expansion must be similar for the coating and the substrate. This parameter get to be critical when coating large parts (several millimetrers). For many medical devices such as heart valve and orthopedic applications, graphite is the sutible substrate.It has excellent hemocompatibility and high mechanical characteristics [29, 16].

For orthopedic implants, coatings of pyrolytic carbon can be minimize many imperfections as wear, wear particle obstetrics, osteolysis and aseptic loosening. Pyrolytic carbon can be extending implants useful lifeimes. The perfect suitability of pyrolytic carbon with the native cartilage and bone joint tissues qualifies fusty hemi-arthroplasty replacements as an substitutional to total joint replacement [17]. When using graphite as substrate is made by composing homogeneous isotropic conglomerate of accurate graphie grains (5mm) blend with homogenized tungsten powder to grant it enough radiopacity. Pyrolytic carbon coating is fully radiolucent thus necessary addition of tungsten [12].

For biomedical devices, there are three kinds of carbon using:low –temperature form of pyrolytic carbon, glassy (vitreous) carbon, and ultra low-temperature isotropic (ULTI) form of vapour deposited carbon. They have a chaotic lattice structure and collectively indicated as turbostratic carbon [21].The important properties of glassy carbon, vapour deposited carbon, silicon doped low temperature isotropic carbon (LTI) pyrolytic carbon and low temperature isotropic (LTI) pyrolytic carbon as explained in table(1). The low temperature isotropic (LTI) pyrolytic carbon is the most kind of pyrolytic carbon used in biomedical applications. Silicon is used as a doping agent to enhance the mechanical properties of pyrolytic carbon[30].

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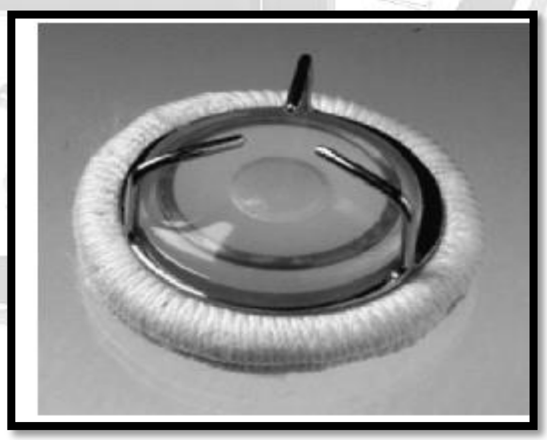
Table(1): The properties of different phases of carbon for bio-applicationa [21, 30]

Property	Glassy carbon	Vapour deposited carbon	LTI pyrolytic carbon	LTI pyrolytic carbon –with silicon
Density g/cm^3	1.4-1.6	1.5-2.2	1.7-2.2	2.04-2.13
Crystallite size (°A)	10-40	8-15	30-40	30-40
Flexural strength (*1000psi)	10-30	50;100	40-80	80-90
Young's modulus(*10^6psi)	3.5-4.5	2-3	2.5-4	4-4.5
Strain to fracture(%)	0.8-1.3	2;5	1.6-2.1	2
Fatigue limit/fracture strength 1	1	1	1	1
Strain energy to fracture (*100psi)	1-2	10	4-8	8
Hardness, DPH	150-200	150-250	150-250	230-370

6-Biomedcal Applications of Pyrolytic Carbon:- The important biomedical applications of pyrolytic carbon are: 1. **Heart Valves**:There are two kinds of heart valves:a-Mechanical hert valves: they are prepared from materials of synthetic origin such as metals,polymers,ceramics.b-Bilogical valves: utilize extra to artificial materials.After proper adjustment by using physic-chemical processing to the materials of biological origin [9]. Figure(7) represents types of mechanical hert valves.

(a) Starr–Edwards silicone rubber ball in metallic cage (1964)



(b) Cross Jones polymeric lenticular poppet in metallic cage (1967)

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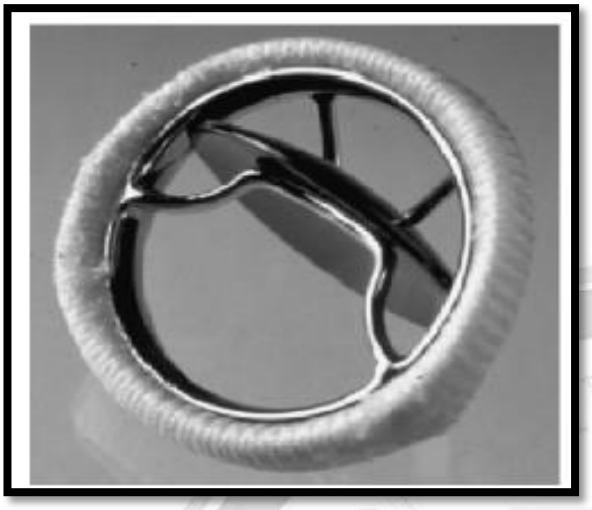
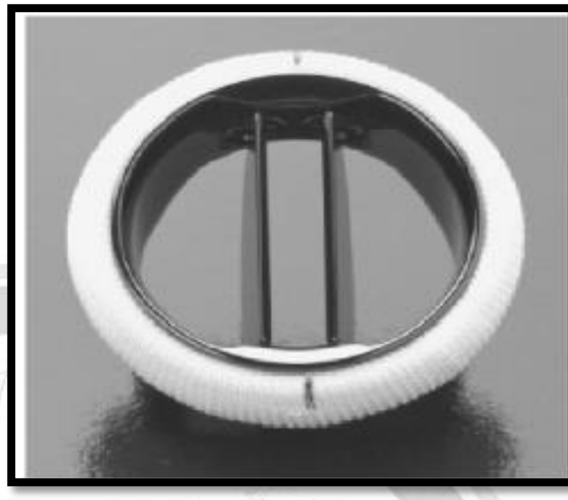


(c) **Bjork Shiley tilting disk, originally a polyacetyl disk in a metallic cage (1969) shown here with a PyC disk (1975)**



(d) **On-X prosthetic heart valve, all-carbon bileaflet valve (1996)**

Figure (7): Types of mechanical heart valves [28]

2.Orthopedic Applications:

Pyrolytic carbon is regarded stellar material for orthopedic application for its characterstic over metallic alloys and polymers as: modulus of elasticity is identical to bone and that decrease the stresss shielding, superb wear resistance, stellar fatigue enduranc, premium biocompatibility with bone and hard tissue, fixation by bone apposition, and, prime biocompatibility with cartilage [17]. Figure (8)represents the bioimplants of pyrolytic carbon in hand.

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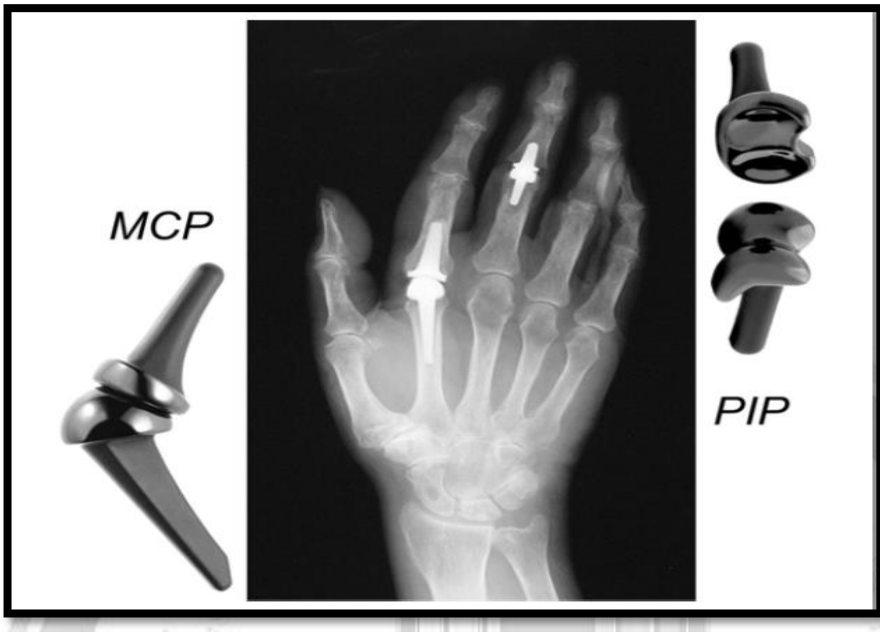
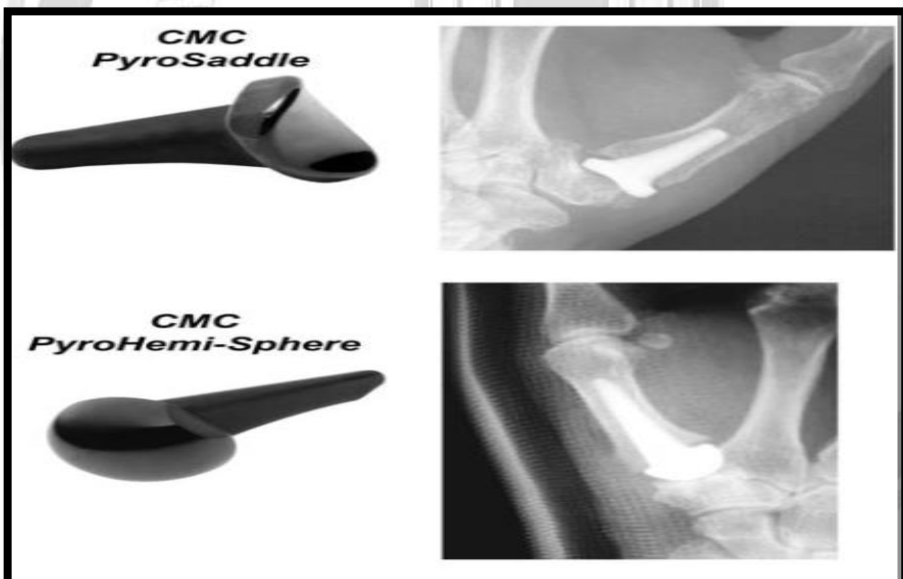


(a)



(b)

Figure (8):Bio implants in hand: (a) X ray of hand contains MCP and PIP from pyrolytic carbon,(b) Hemiarthroplasty CMC implants from [17]

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8- Conclusions:

The excellent properties of pyrolytic carbon which make it as one of biomaterials. The present paper has focused on principles of production this material and biomedical applications. The most important conclusions can be summed up in the following way:

-Pyrolytic carbon can be deposited by chemical vapour deposition CVD with pyrolysis process.

-Necessary for coating higher than 1 mm in thichness using substrate of carbon to reduce the diffrence in themal cofficient of expansion.

-The substrate of graphite for heart valves and orthopedic applications is needed fine particles of tungsten to make X-ray clear because pure pyrolytic carbon is radio-transparent.

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JOURNAL OF UNIVERSITY OF BABYLON

For ENGINEERING SCIENCES (JUBES)

Vol.30, No.3.| 2022

اساسيات الانتاج و التطبيقات للبايروليتك كاربون كمادة حياتية

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الخلاصة

التطور الحاصل في الجراحة الحديثة يرتبط بشكل خاص مع توسع المواد الحياتية. من الامثلة على التطبيقات للمواد الحياتية العدد المستخدمة في تثبيت الكسر الداخلي والجراحة الترقيعية للمفاصل و جراحة الشرايين و ابدال صمامات القلب. اهتمام كبير بالمواد الكاربونية لاستخدامها في التطبيقات الحياتية بسبب امتلاكها للتوافقية الحياتية ومقاومة البلى والخواص الميكانيكية المتميزة. جميع هذه الخواص تتوفر في البايروليتك كاربون. لا تتواجد هذه المادة في الطبيعة انما هي من صنع الانسان. الترسيب الكيميائي للبخار هي الطريقة الوحيدة للحصول عليه. صمامات القلب الميكانيكية و التطبيقات المتعلقة بالعظام مثل زروعات اليد و الرسغ يتم تصنيعها من مادة البايروليتك كاربون. في هذا البحث يتم وصف طريقة التصنيع و الخواص و التطبيقات الحياتية للبايروليتك كاربون.

الكلمات الدالة : بايروليتك كاربون، الترسيب الكيميائي للبخار، انحلال حراري، مواد حياتية.

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