CHAPTER 1

INTRODUCTION TO COMPOSITE MATERIAL

1.1 INTRODUCTION

Mankind has been aware composite materials since several hundred years before Christ and applied innovation to improve the quality of life. Although it is not clear has to how Man understood the fact that mud bricks made sturdier houses if lined with straw, he used them to make buildings that lasted.

Ancient Pharaohs made their slaves use bricks with to straw to enhance the structural integrity of their buildings, some of which testify to wisdom of the dead civilization even today.

Contemporary composites results from research and innovation from past few decades have progressed from glass fiber for automobile bodies to particulate composites for aerospace and a range other applications.

Ironically, despite the growing familiarity with composite materials and ever-increasing range of applications, the term defines a clear definition. Loose terms like “materials composed of two or more distinctly identifiable constituents” are used to describe natural composites like timber, organic materials, like tissue surrounding the skeletal system, soil aggregates, minerals and rock.

Historical examples of composites are abundant in the literature. Significant examples include the use of reinforcing mud walls in houses with bamboo shoots, glued laminated wood by Egyptian (1500 BC), and laminated metals in forging swords (1800 AD). In the 20th century, modern composites were used in the 1930s where glass fibers reinforced resins. Boats and aircrafts were built out of these glass composites, commonly called fiberglass. Since the 1970s, application of composites has widely increased due to development of new fibers such as carbon, boron, and aramids, and new composite systems with matrices made of metals and ceramics.

1.2 COMPOSITES

A typical composite material is a system of materials composing of two or more materials (mixed and bonded) on macroscopic scale.

Generally, a composite material is composed of reinforcement (fibers, particles, flakes and/or fillers) embedded in a matrix (polymers, metals or ceramics). The matrix holds the reinforcement to form the desired shape while the reinforcement improves the overall mechanical properties of the matrix. When designed properly, the new combined material exhibit better strength than would each individual material.

As defined by Jartiz, Composite are multifunctional material system that provide characteristics not obtainable from any discrete material. They are cohesive structures made by physically combining two or more compatible materials, different in composition and characteristics and sometimes in form.

Kelly very clearly stresses that the composites should not be regarded simple as a combining of two materials. In broader significance: the combination has its own distinctive properties. In terms of strength or resistance to heat some other desirable quality, it is better than either of the component alone or radically different from either of them.

Berghezan defines as “The composites are compound materials which differ from alloys by the fact that the individual components retain their characteristics but are so incorporated into the composite as to take advantage only of their attributes and not of their shortcomings”, in order to obtain an improved material.

Van Suchetelan explains composite materials as heterogeneous materials consisting of two or more solid phases, which are in intimate contact with each other on a microscopic scale. They can be also considered as homogeneous materials on a microscopic scale in the sense that any portion of it will have the same physical property.

1.3 CHARACTERISTICS OF COMPOSITES

Composites consist of one or more discontinuous phases embedded in continuous phase. The discontinuous phase is usually harder and stronger than the continuous phase and is called the ‘reinforcement’ or ‘reinforcing material’, whereas the continuous phase is termed as the ‘matrix’.

Properties of composites are strongly dependent on the properties of their constituent materials their distribution and the interaction among them. The composite properties may be the volume fraction sum of the properties of the constituents or the constituents may interact in a synergistic way resulting in improved or better properties. Apart from the nature of the constituent materials, the geometry of the reinforcement (shape, size and size distribution) influences the properties of the composite to a great extent. The concentration distribution and orientation of the reinforcement also affect the properties.

The phase of the discontinuous phase (which may by spherical, cylindrical, or rectangular cross-sanctioned prism or platelets), the size and size distribution (which controls the texture of the material) and volume fraction determine the interfacial area, which plays an important role in determining the extent of the interaction between the reinforcement and the matrix.

Concentration, usually measured as volume or weight fraction, determine the contribution of a single constituent to the overall properties of the composites. It is not only the single most important parameter influencing the properties of the composites, but also an easily controllable manufacturing variable used to alter its properties. The orientation of the reinforcement affects the isotropy of the system.

1.4 CLASSIFICATION OF COMPOSITES

Composite materials can be classified in different ways. Classification based on the geometry of a representative unit of reinforcement is convenient since it is the geometry of the reinforcement which is responsible for the mechanical properties and high performance of composites.

The two broad classes of composites are:

(a) Particulate composites

(b) Fibrous composites.

(a). Particulate Composites

As the name itself indicates, the reinforcement is of particle nature (platelets are also included in this class). It may be spherical, cubic, tetragonal, a platelet, or of other regular or irregular shape. In general, particles are not very effective in improving fracture resistance but they enhance the stiffness of the composite to a limited to a limited extent.

(b). Fibrous composites

A fiber is characterized by its length being much greater compared to its cross-sectional dimensions. The dimensions of reinforcement determine its capability of contributing its properties to the matrix since a reinforcement having a long dimension discourages the growth of incipient cracks normal to the reinforcement that might otherwise lead to failure, particularly with brittle matrices.

Fibers, because of their small cross-sectional dimensions, are not directly usable in engineering applications. They, therefore, embedded in matrix materials to form fibrous composites. The matrix serves to bind the fibers together, transfer loads to the fibers, and protect them against environment attack and damage due to handling. In discontinuous fiber reinforced composites, the load transfer function of the matrix is more critical than in continuous fiber composites.

1.5 CLASSIFICATION BASED ON MATRIX

Depending on the matrix used in the composite, composites can be broadly classified as:

- **Polymer-Matrix Composites**
- **Ceramic-Matrix Composites**
- **Metal-Matrix Composites**

All these categories of composites are useful in different areas depending on the applications.

1.5.1 Polymer Matrix Composites (PMCs)

PMCs consist of a polymer as the matrix. These materials are used in greatest diversity of composite applications, as well as in largest quantities, in light of their room-temperature properties, ease of fabrication, and cost. Some of these commonly used reinforcement used in PMCs includes; glass fibers, either, continuous or discontinuous, contained within a polymer matrix. Carbon, which is a high- performance fiber material is the most commonly, used as reinforcement in advanced (i.e., non-fiberglass) polymer-matrix composites. Carbon- reinforced polymer composite are currently being utilized extensively in sports and recreational equipment (fishing rods, golf clubs), pressure vessels, and aircraft structural components – both military and commercial.

1.5.2 Ceramic Matrix Composites (CMCs)

CMCs consist of a ceramic material as a matrix, with particulates, fibers or whiskers as the reinforcement medium. Ceramic materials are inherently resilient to oxidation and deterioration at elevated temperatures. Some of these materials would be ideal candidates for use in high temperature and severe-stress applications, specifically for components in automobile and aircraft gas turbine engines. The fracture toughness of ceramics has been improved significantly by the development of a new generation of ceramic-matrix composites

1.5.3 Metal-Matrix Composites (MMCs)

MMCs are defined as materials consisting of a combination of fibers, whiskers, and particulates embedded in a metallic matrix which could be Al, Mg, Cu, Fe, etc.

The development of metal matrix composites has been driven primarily by the need for structural materials with better specific strength and modulus than monolithic metals, especially at high temperature. These materials demonstrate one of the most intriguing characteristics of composites, which is, the ability to obtained with monolithic materials. As the name implies, in the Metal Matrix Composites, the matrix is a ductile material and reinforcement is a brittle ceramic. These materials can be utilized at high service temperature than their base metal counterparts; furthermore, the reinforcement may improve specific strength, specific stiffness, abrasion resistance, creep resistance, and dimensional stability. The matrix material lends good toughness and high thermal conducting properties to the MMC. Some of the advantages of these materials over the polymer matrix composites include higher operating temperatures, non-flammability, and greater resistance to degradation. Normally the processing of MMCs involves at least two steps: consolidation or synthesis (i.e., introduction of reinforcement into the matrix), followed by a shaping operation. A host of consolidation techniques are available, some of which are relatively sophisticated; particulate

MMCs are amenable to shaping by standard metal-forming operations (e.g., extrusion, forging, rolling) recently, some of the automobile manufacturers have introduced engine components consisting of an aluminum- alloy matrix that is reinforced with alumina and carbon fiber s; this MMC is light in weight and resist wear and thermal distortion. Aerospace structural applications include advanced aluminum-alloy metal-matrix composites; boron fibers are used as the reinforcement for the Space Shuttle Orbiter, and continuous graphite fibers for the Hubble telescope.

1.6 MATRIX MATERIALS

Composites cannot be made from constituents with divergent linear expansion characteristics. The interface is the area of contact between the reinforcement and the matrix materials. In some cases, the region is a distinct added phase. Whenever there is interphase, there has to be two interphases between each side of the interphase and its adjoint constituent. Some composites provide interphases when surfaces dissimilar constituents interact with each other. Choice of fabrication method depends on matrix properties and the effect of matrix on properties of reinforcements. One of the prime considerations in the selection and fabrication of composites is that the constituents should be chemically inert non-reactive. Figure 1.1 helps to classify matrices.

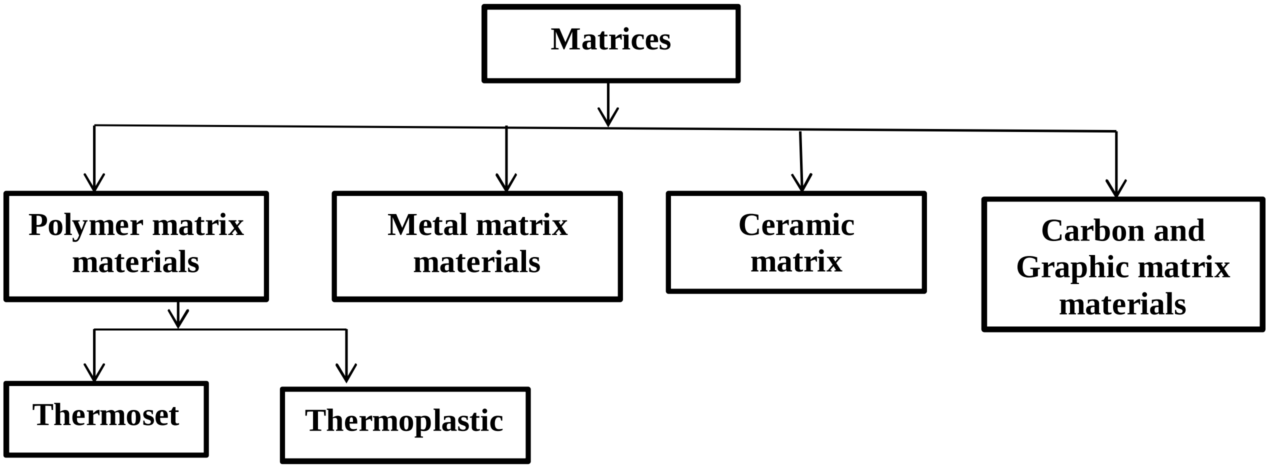


Figure 1.1: Classification of matrices

1.6.1 Polymer Matrix Materials

Polymers make ideal materials as they can be processed easily, possess lightweight, and desirable mechanical properties. It follows, therefore, that high temperature resins are extensively used in aeronautical applications.

Two main kinds of polymers are thermosets and thermoplastics. Thermosets have qualities such as a well-bonded three-dimensional molecular structure after curing. They decompose instead of melting on hardening. Merely changing the basic composition of the resin is enough to alter the conditions suitably for curing and determine its other characteristics. They can be retained in a partially cured condition too over prolonged periods of time, rendering Thermosets very flexible. Thus, they are most suited as matrix bases for advanced conditions fiber reinforced composites. Thermosets find wide ranging applications in the chopped fiber composites form particularly when a premixed or moulding compound with fibers of specific quality and aspect ratio happens to be starting material as in epoxy, polymer and phenolic polyamide resins.

Thermoplastics have one- or two-dimensional molecular structure and they tend to at an elevated temperature and show exaggerated melting point. Another advantage is that the process of softening at elevated temperatures can reversed to regain its properties during cooling, facilitating applications of conventional compress techniques to mould the compounds.

Resins reinforced with thermoplastics now comprised an emerging group of composites. The theme of most experiments in this area to improve the base properties of the resins and extract the greatest functional advantages from them in new avenues, including attempts to replace metals in die-casting processes. In crystalline thermoplastics, the reinforcement affects the morphology to a considerable extent, prompting the reinforcement to empower nucleation. Whenever crystalline or amorphous, these resins possess the facility to alter their creep over an extensive range of temperature. But this range includes the point at which the usage of resins is constrained, and the reinforcement in such systems can increase the failure load as well as creep resistance. Figure 1.2 shows kinds of thermoplastics.

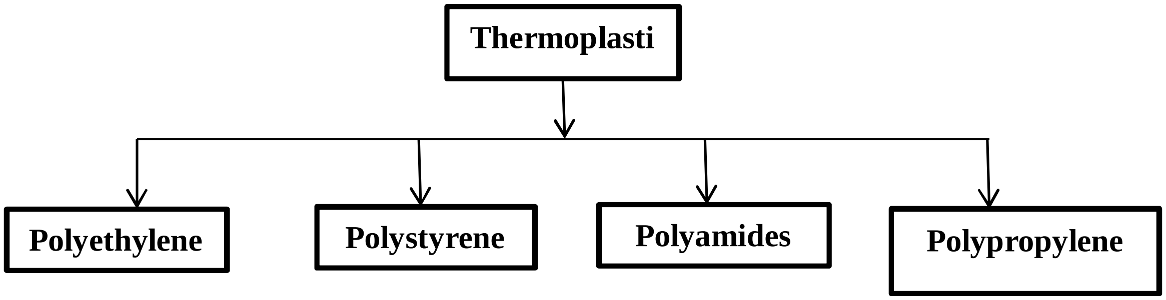


Figure 1.2: Kinds of thermoplastics

A small quantum of shrinkage and the tendency of the shape to retain its original form are also to be accounted for. But reinforcements can change this condition too. The advantage of thermoplastics systems over thermosets are that there are no chemical reactions involved, which often result in the release of gases or heat. Manufacturing is limited by the time required for heating, shaping and cooling the structures.

Thermoplastics resins are sold as moulding compounds. Fiber reinforcement is apt for these resins. Since the fibers are randomly dispersed, the reinforcement will be almost isotropic. However, when subjected to moulding processes, they can be aligned directionally.

There are a few options to increase heat resistance in thermoplastics. Addition of fillers raises the heat resistance. But all thermoplastic composites tend loose their strength at elevated temperatures. However, their redeeming qualities like rigidity, toughness and ability to repudiate creep, place thermoplastics in the important composite materials bracket. They are used in automotive control panels, electronic products encasement etc.

Newer developments augur the broadening of the scope of applications of thermoplastics. Huge sheets of reinforced thermoplastics are now available and they only require sampling and heating to be moulded into the required shapes. This has facilitated easy fabrication of bulky components, doing away with the more cumbersome moulding compounds.

Thermosets are the most popular of the fiber composite matrices without which, research and development in structural engineering field could get truncated. Aerospace components, automobile parts, defense systems etc., use a great deal of this type of fiber composites.

Epoxy matrix materials are used in printed circuit boards and similar areas. Figure 1.3 shows some kinds of thermosets.

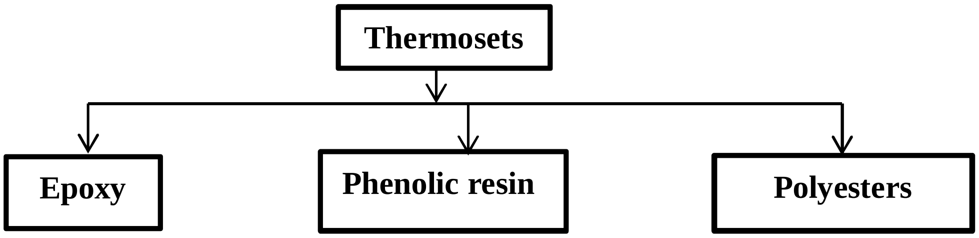


Figure 1.3: Kinds of thermoset

Direct condensation Polymerization followed by rearrangement reactions to form heterocyclic entities is the method generally used to produce thermoset resins. Water, a product of the reaction, in both methods, hinders production of void-free composites. These voids have a negative effect on properties of the composites in terms of strength and dielectric properties.

Polyesters phenolic and Epoxies are the two important classes of thermoset resins. Epoxy resins are widely used in filament-wound composites and are suitable for moulding prepress.

They are reasonably stable to chemical attacks and are excellent adherents having slow shrinkage during curing and no emission of volatile gases. These advantages, however, make the use of epoxies rather expensive. Also, they cannot be expected beyond a temperature of 140ºC. Their use in high technology areas where service temperatures are higher, as a result, is ruled out.

Polyester resins on the other hand are quite easily accessible, cheap and find use in a wide range of fields. Liquid polyesters are stored at room temperature for months, sometimes for years and the mere addition of a catalyst can cure the matrix material within a short time. They are used in automobile and structural applications. The cured polyester is usually rigid or flexible as the case may be and transparent. Polyesters withstand the variations of environment and stable against chemicals. Depending on the formulation of the resin or service requirement of application, they can be used up to about 75ºC or higher. Other advantages of polyesters include easy compatibility with few glass fibers and can be used with verify of reinforced plastic accountrey.

Aromatic Polyamides are the most sought after candidates as the matrices of advanced fiber composites for structural applications demanding long duration exposure for continuous service at around 200 - 250º C .

1.6.2 Metal Matrix Materials

Metal matrix composites, at present though generating a wide interest in research fraternity, are not as widely in use as their plastic counterparts. High strength, fracture toughness and stiffness are offered by metal matrices than those offered by their polymer counterparts. They can withstand elevated temperature in corrosive environment than polymer composites. Most metals and alloys could be used as matrices and they require reinforcement materials which need to be stable over a range of temperature and non-reactive too. However the guiding aspect for the choice depends essentially on the matrix material. Light metals form the matrix for temperature application and the reinforcements in addition to the aforementioned reasons are characterized by high moduli.

Most metals and alloys make good matrices. However, practically, the choices for low temperature applications are not many. Only light metals are responsive, with their low density proving an advantage. Titanium, Aluminium and magnesium are the popular matrix metals currently in vogue, which are particularly useful for aircraft applications. If metallic matrix materials have to offer high strength, they require high modulus reinforcements. The strength-to-weight ratios of resulting composites can be higher than most alloys. The melting point, physical and mechanical properties of the composite at various temperatures determine the service temperature of composites. Most metals, ceramics and compounds can be used with matrices of low melting point alloys. The choice of reinforcements becomes more stunted with increase in the melting temperature of matrix materials.

1.6.3 Ceramic Matrix Materials

Ceramics can be described as solid materials which exhibit very strong ionic bonding in general and in few cases covalent bonding. High melting points, good corrosion resistance, stability at elevated temperatures and high compressive strength, render ceramic-based matrix materials a favourite for applications requiring a structural material that doesn’t give way at temperatures above 1500ºC. Naturally, ceramic matrices are the obvious choice for high temperature applications. High modulus of elasticity and low tensile strain, which most ceramics posses, have combined to cause the failure of attempts to add reinforcements to obtain strength improvement. This is because at the stress levels at which ceramics rupture, there is insufficient elongation of the matrix which keeps composite from transferring an effective quantum of load to the reinforcement and the composite may fail unless the percentage of fiber volume is high enough. A material is reinforcement to utilize the higher tensile strength of the fiber, to produce an increase in load bearing capacity of the matrix. Addition of high-strength fiber to a weaker ceramic has not always been successful and often the resultant composite has proved to be weaker. The use of reinforcement with high modulus of elasticity may take care of the problem to some extent and presents pre-stressing of the fiber in the ceramic matrix is being increasingly resorted to as an option. When ceramics have a higher thermal expansion coefficient than reinforcement materials, the resultant composite is unlikely to have a superior level of strength. In that case, the composite will develop strength within ceramic at the time of cooling resulting in microcracks extending from fiber to fiber within the matrix. Microcracking can result in a composite with tensile strength lower than that of the matrix.

1.6.4 Carbon Matrices

Carbon and graphite have a special place in composite materials options, both being highly superior, high temperature materials with strengths and rigidity that are not affected by temperature up to 2300ºC. This carbon-carbon composite is fabricated through compaction of carbon or multiple impregnations of porous frames with liquid carboniser precursors and subsequent pyrolization. They can also be manufactured through chemical vapour deposition of pyrolytic carbon. Carbon-carbon composites are not be applied in elevated temperatures, as many composites have proved to be far superior at these temperatures. However, their capacity to retain their properties at room temperature as well as at temperature in the range of 2400ºC and their dimensional stability make them the oblivious choice in a garnut of applications related to aeronautics, military, industry and space. Components, that are exposed to higher temperature and on which the demands for high standard performance are many, are most likely to have carbon-carbon composites used in them.

1.6.5 Glass Matrices

In comparison to ceramics and even considered on their own merit, glass matrices are found to be more reinforcement-friendly. The various manufacturing methods of polymers can be used for glass matrices. Glasses are meant to improve upon performance of several applications. Glass matrix composite with high strength and modulus can be obtained and they can be maintained upto temperature of the order of 650ºC. Composites with glass matrices are considered superior in dimensions to polymer or metal system, due to the low thermal expansion behaviour. This property allows fabrication of many components in intricate shapes and their tribological characters are considered very special. Since the elastic modulus of glass is far lower than of any prospective reinforcement materials, application of stress usually results in high elasticity modulus fiber that the tensile strength of the composite its considerably enhanced than that of the constituents, which is not case in ceramic matrices.

1.7 REINFORCEMENT

Reinforcements for the composites can be fibers, fabrics particles or whiskers. Fibers are essentially characterized by one very long axis with other two axes either often circular or near circular. Particles have no preferred orientation and so does their shape. Whiskers have a preferred shape but are small both in diameter and length as compared to fibers. Figure 1.4 shows types of reinforcements in composites.

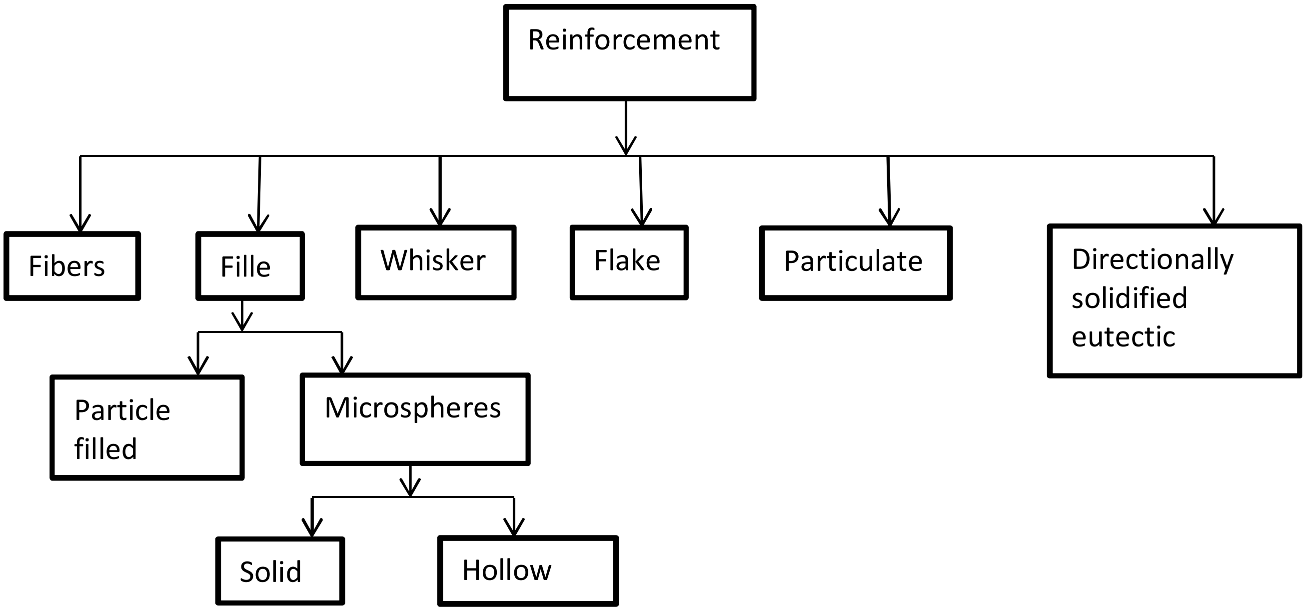


Figure 1.4: Types of reinforcement

Reinforcing constituents in composites, as the word indicates, provide the strength that makes the composite what it is. But they also serve certain additional purposes of heat resistance or conduction, resistance to corrosion and provide rigidity. Reinforcement can be made to perform all or one of these functions as per the requirements. A reinforcement that embellishes the matrix strength must be stronger and stiffer than the matrix and capable of changing failure mechanism to the advantage of the composite. This means that the ductility should be minimum or even nil the composite must behave as brittle as possible

1.7.1 Fibers

Fibers are the important class of reinforcements, as they satisfy the desired conditions and transfer strength to the matrix constituent influencing and enhancing their properties as desired. Glass fibers are the earliest known fibers used to reinforce materials. Ceramic and metal fibers were subsequently found out and put to extensive use, to render composites stiffer more resistant to heat. Fibers fall short of ideal performance due to several factors. The performance of a fiber composite is judged by its length, shape, orientation, composition of the fibers and the mechanical properties of the matrix.

The orientation of the fiber in the matrix is an indication of the strength of the composite and the strength is greatest along the longitudinal directional of fiber. This doesn’t mean the longitudinal fibers can take the same quantum of load irrespective of the direction in which it is applied. Optimum performance from longitudinal fibers can be obtained if the load is applied along its direction. The slightest shift in the angle of loading may drastically reduce the strength of the composite.

Unidirectional loading is found in few structures and hence it is prudent to give a mix of orientations for fibers in composites particularly where the load is expected to be the heaviest.

Monolayer tapes consisting of continuous or discontinuous fibers can be oriented unidirectional stacked into plies containing layers of filaments also oriented in the same direction. More complicated orientations are possible too and nowadays, computers are used to make projections of such variations to suit specific needs. In short, in planar composites, strength can be changed from unidirectional fiber oriented composites tha result in composites with nearly isotropic properties.

Properties of angle-plied composites which are not quasi-isotropic may vary with the number of plies and their orientations. Composite variables in such composites are assumed to have a constant ratio and the matrices are considered relatively weaker than the fibers. The strength of the fiber in any one of the three axes would, therefore be one-third the unidirectional fiber composite, assuming that the volume percentage is equal in all three axes. However, orientation of short fibers by different methods is also possible like random orientations by sprinkling on to given plane or addition of matrix in liquid or solid state before or after the fiber deposition. Even three-dimensional orientations can achieved in this way. There are several methods of random fiber orientations, which in a two-dimensional one, yield composites with one-third the strength of an unidirectional fiber-stressed composite, in the direction of fibers. In a 3-dimension, it would result in a composite with a comparable ratio, about less than one-fifth. In very strong matrices, moduli and strengths have not been observed. Application of the strength of the composites with such matrices and several orientations is also possible. The longitudinal strength can be calculated on the basis of the assumption that fibers have been reduced to their effective strength on approximation value in composites with strong matrices and non-longitudinally orientated fibers. It goes without saying that fiber composites may be constructed with either continuous or short fibers. Experience has shown that continuous fibers (or filaments) exhibit better orientation, although it does not reflect in their performance. Fibers have a high aspect ratio, i.e., their lengths being several times greater than their effective diameters. This is the reason why filaments are manufactured using continuous process. This finished filaments.

Mass production of filaments is well known and they match with several matrices in different ways like winding, twisting, weaving and knitting, which exhibit the characteristics of a fabric. Since they have low densities and high strengths, the fiber lengths in filaments or other fibers yield considerable influence on the mechanical properties as well as the response of composites to processing and procedures. Shorter fibers with proper orientation composites that use glass, ceramic or multi- purpose fibers can be endowed with considerably higher strength than those that use continuous fibers. Short fibers are also known to their theoretical strength. The continuous fiber constituent of a composite is often joined by the filament winding process in which the matrix impregnated fiber wrapped around a mandrel shaped like the part over which the composite is to be placed, and equitable load distribution and favorable orientation of the fiber is possible in the finished product. However, winding is mostly confined to fabrication of bodies of revolution and the occasional irregular, flat surface.Short-length fibers incorporated by the open- or close-mould process are found to be less efficient, although the input costs are considerably lower than filament winding. Most fibers in use currently are solids which are easy to produce and handle, having a circular cross-section, although a few non-conventional shaped and hollow fibers show signs of capabilities that can improve the mechanical qualities of the composites.

Given the fact that the vast difference in length and effective diameter of the fiber are assets to a fiber composite, it follows that greater strength in the fiber can be achieved by smaller diameters due to minimization or total elimination of surface of surface defects. After flat-thin filaments came into vogue, fibers rectangular cross sections have provided new options for applications in high strength structures. Owing to their shapes, these fibers provide perfect packing, while hollow fibers show better structural efficiency in composites that are desired for their stiffness and compressive strengths. In hollow fibers, the transverse compressive strength is lower than that of a solid fiber composite whenever the hollow portion is more than half the total fiber diameter. However, they are not easy to handle and fabricate.

1.7.2 Whiskers

Single crystals grown with nearly zero defects are termed whiskers. They are usually discontinuous and short fibers of different cross sections made from several materials like graphite, silicon carbide, copper, iron etc. Typical lengths are in 3 to 55 nm ranges. Whiskers differ from particles in that, whiskers have a definite length to width ratio greater than one. Whiskers can have extraordinary strengths upto 7000 MPa. Whiskers were grown quite incidentally in laboratories for the first time, while nature has some geological structures that can be described as whiskers. Initially, their usefulness was overlooked as they were dismissed as incidental by-products of other structure. However, study on crystal structures and growth in metals sparked off an interest in them, and also the study of defects that affect the strength of materials, they came to be incorporated in composites using several methods, including power metallurgy and slip-casting techniques. Metal-whisker combination, strengthening the system at high temperatures, has been demonstrated at the laboratory level. But whiskers are fine, small sized materials not easy to handle and this comes in the way of incorporating them into engineering materials to come out with a superior quality composite system. Early research has shown that whisker strength varies inversely with effective diameter. When whiskers were embedded in matrices, whiskers of diameter upto 2 to 10µm yielded fairly good composites. Ceramic material’s whiskers have high moduli, useful strengths and low densities. Specific strength and specific modulus are very high and this makes ceramic whiskers suitable for low weight structure composites. They also resist temperature, mechanical damage and oxidation more responsively than metallic whiskers, which are denser than ceramic whiskers. However, they are not commercially viable because they are damaged while handling.

1.7.3 Laminar Composites

Laminar composites are found in as many combinations as the number of materials. They can be described as materials comprising of layers of materials bonded together. These may be of several layers of two or more metal materials occurring alternately or in a determined order more than once, and in as many numbers as required for a specific purpose. Clad and sandwich laminates have many areas as it ought to be, although they are known to follow the rule of mixtures from the modulus and strength point of view. Other intrinsic values pertaining to metal- matrix, metal-reinforced composites are also fairly well known. Powder metallurgical processes like roll bonding, hot pressing, diffusion bonding, brazing and so on can be employed for the fabrication of different alloys of sheet, foil, powder or sprayed materials. It is not possible to achieve high strength materials unlike the fiber version. But sheets and foils can be made isotropic in two dimensions more easily than fibers. Foils and sheets are also made to exhibit high percentages of which they are put. For instance, a strong sheet may use over 92% in laminar structure, while it is difficult to make fibers of such compositions. Fiber laminates cannot over 75% strong fibers. The main functional types of metal-metal laminates that do not posses high strength or stiffness are single layered ones that endow the composites with special properties, apart from being cost-effective. They are usually made by pre-coating or cladding methods. Pre-coated metals are formed by forming by forming a layer on a substrate, in the form of a thin continuous film. This is achieved by hot dipping and occasionally by chemical plating and Electroplating. Clad metals are found to be suitable for more intensive environments where denser faces are required. There are many combinations of sheet and foil which function as adhesives at low temperatures. Such materials, plastics or metals, may be clubbed together with a third constituent. Pre-painted or pre- finished metal whose primary advantage is elimination of final finishing by the user is the best known metal-organic laminate. Several combinations of metal-plastic, vinyl-metal laminates, organic films and metals, account for upto 95% of metal-plastic laminates known. They are made by adhesive bonding processes.

1.7.4 Flake Composites

Flakes are often used in place of fibers as can be densely packed. Metal flakes that are in close contact with each other in polymer matrices can conduct electricity or heat, while mica flakes and glass can resist both. Flakes are not expensive to produce and usually cost less than fibers. But they fall short of expectations in aspects like control of size, shape and show defects in the end product. Glass flakes tend to have notches or cracks around the edges, which weaken the final product. They are also resistant to be lined up parallel to each other in a matrix, causing uneven strength. They are usually set in matrices, or more simply, held together by a matrix with a glue-type binder. Depending on the end-use of the product, flakes are present in small quantities or occupy the whole composite. Flakes have various advantages over fibers in structural applications. Parallel flakes filled composites provide uniform mechanical properties in the same plane as the flakes. While angle-plying is difficult in continuous fibers which need to approach isotropic properties, it is not so in flakes. Flake composites have a higher theoretical modulus of elasticity than fiber reinforced composites. They are relatively cheaper to produce and be handled in small quantities.

1.7.5 Filled Composites

Filled composites result from addition of filer materials to plastic matrices to replace a portion of the matrix, enhance or change the properties of the composites. The fillers also enhance strength and reduce weight.

Another type of filled composite is the product of structure infiltrated with a second-phase filler material. The skeleton could be a group of cells, honeycomb structures, like a network of open pores. The infiltrant could also be independent of the matrix and yet bind the components like powders or fibers, or they could just be used to fill voids. Fillers produced from powders are also considered as particulate composite. In the open matrices of a porous or spongy composite, the formation is the natural result of processing and such matrices can be strengthened with different materials. Metal impregnates are used to improve strength or tolerance of the matrix. Metal casting, graphite, powder metallurgy parts and ceramics belong to this class of filled composites.

In the honeycomb structure, the matrix is not naturally formed, but specifically designed to a predetermed shape. Sheet materials in the hexagonal shapes are impregnated with resin or foam and are used as a core material in sandwich composites. Fillers may be the main ingredient or an additional one in a composite. The filler particles may be irregular structures, or have precise geometrical shapes like polyhedrons, short fibers or spheres.

While their purpose is far from adding visual embellishment to the composites, they occasionally impart colour or opacity to the composite which they fill. As inert additives, fillers can change almost any basic resin characteristic in all directions required, to tide over the many limitations of basic resins as far as composites are concerned. The final composite properties can be affected by the shape, surface treatment, blend of particle types, size of the particle in the filler material and the size distribution. Filled plastics tend to behave like two different constituents. They do not alloy and accept the bonding. They are meant to develop mutually; they desist from interacting chemically with each other. It is vital that the constituents remain in co-ordination and do not destroy each others desired properties. Matrix in a few filled composites provides the main framework while the filler furnishes almost all desired properties. Although the matrix forms the bulk of the composite, the filler material is used in such great quantities relatively that it becomes the rudimentary constituent. The benefits offered by fillers include increase stiffness, thermal resistance, stability, strength and abrasion resistance, porosity and a favorable coefficient of thermal expansion. However, the methods of fabrication are very limited and the curing of some resins is greatly inhibited. They also shorten the life span of some resins and are known to weaken a few composites.

1.7.6 Particulate Reinforced Composites

Microstructures of metal and ceramics composites, which show particles of one phase strewn in the other, are known as particle reinforced composites. Square, triangular and round shapes of reinforcement are known, but the dimensions of all their sides are observed to be more or less equal. The size and volume concentration of the dispersoid distinguishes it from dispersion hardened materials. The dispersed size in particulate composites is of the order of a few microns and volume concentration is greater than 28%. The difference between particulate composite and dispersion strengthened ones is, thus, oblivious. The mechanism used to strengthen each of them is also different. The dispersed in the dispersion-strengthen materials reinforces the matrix alloy by arresting motion of dislocations and needs large forces to fracture the restriction created by dispersion. In particulate composites, the particles strengthen the system by the hydrostatic coercion of fillers in matrices and by their hardness relative to the matrix. Three-dimensional reinforcement in composites offers isotropic properties, because of the three systematical orthogonal planes. Since it is not homogeneous, the material properties acquire sensitivity to the constituent properties, as well as the interfacial properties and geometric shapes of the array. The composite's strength usually depends on the diameter of the particles, the inter-particle spacing, and the volume fraction of the reinforcement. The matrix properties influence the behaviour of particulate composite too.

1.7.7 Cermets

Cermets are one of the premier groups of particle strengthened comp osites and usually comprises ceramic grains of borides, carbides or oxides. The grains are dispersed in a refractory ductile metal matrix, which accounts for 20 to 85% of the total volume. The bonding between ceramic and metal constituents is the result of a small measure of mutual solutions. Metal oxide systems show poor bonding and require additional bonding agents. Cermet structures are usually produced using power metallurgy techniques. Their potential properties are several and varied depending on the relative volumes and compositions and of the metal and ceramic constituents. Impregnation of a porous ceramic structure with a metallic matrix binder is another method used to produce cermets. Cermets may be employed as coating in a power form. The power is sprayed through a gas flame and fused to a base material. A wide variety of cermets have been produced on a small scale, but only a few have appreciable value commercially.

1.7.8 Microspheres

Microspheres are considered to be some of the most useful fillers. Their specific gravity, stable particle size, strength and controlled density to modify products without compromising on profitability or physical properties are its their most-sought after assets. Solid glass Microspheres, manufactured from glass are most suitable for plastics. Solid glass Microspheres are coated with a binding agent which bonds itself as well as the sphere’s surface to the resin. This increases the bonding strength and basically removes absorption of liquids into the separations around the spheres.

Solid Microspheres have relatively low density, and therefore, influence the commercial value and weight of the finished product. Studies have indicated that their inherent strength is carried over to the finished moulded part of which they form a constituent.

Hollow microspheres are essentially silicate based, made at controlled specific gravity. They are larger than solid glass spheres used in polymers and commercially supplied in a wider range of particle sizes. Commercially, silicate-based hollow microspheres with different compositions using organic compounds are also available. Due to the modification, the microspheres are rendered less sensitive to moisture, thus reducing attraction between particles. This is very vital in highly filled liquid polymer composites where viscosity enhancement constraints the quantum of filler loading.

Formerly, hollow spheres were mostly used for thermosetting resin systems. Now, several new strong spheres are available and they are at least five times stronger than hollow microspheres in static crush strength and four times long lasting in shear. Recently, ceramic alumino silicate microspheres have been introduced in thermoplastic systems. Greater strength and higher density of this system in relation to siliceous microspheres and their resistance to abrasions and considerable strength make then suitable for application in high pressure conditions. Hollow microspheres have a lower specific gravity than the pure resin. This makes it possible to use them for lightning resin dominant compounds. They find wide applications in aerospace and automotive industries where weight reduction for energy conservation is one of the main considerations. But their use in systems requiring high shear mixing or high-pressure moulding is restricted as theircrush resistance is in no way comparable to that of solid spheres. Fortunately, judicious applications of hollow spheres eliminate crazing at the bends in the poly-vinyl chloride plastisol applications, where the end component is subjected to bending stresses. Microspheres, whether solid or hollow, show properties that are directly related to their spherical shape let them behave like minute ball bearing, and hence, they give better flow properties. They also distribute stress uniformly throughout resin matrices. In spherical particles, the ratio of surface area to volume is minimum. In resin-rich surfaces of reinforced systems, the microspheres which are free of orientation and sharp edges are capable of producing smooth surfaces.

1.7.9 Solidification of Composites

Directional solidification of alloys is adopted to produce in-situ fibers. They are really a part of the alloy being precipitated from the melt, while the alloy is solidifying. This comprises eutectic alloys wherein the molten material degenerates to form many phases at a steady temperature. When the reaction is carried out after ensuring the solidifying phases, directionally solidified eutectics result.

During the solidification of alloy, crystals nucleate from the mould or some relatively cooler region. A structure with many crystalline particles or grains results from this and grows into each other. When unidirectionallly solidified, random coalescing is not allowed to occur.

1.8: ADVANTAGES OF COMPOSITES

- High resistance to fatigue and corrosion degradation.
- High ‘strength or stiffness to weight’ ratio. As enumerated above, weight savings are significant ranging from 25-45% of the weight of conventional metallic designs.
- Directional tailoring capabilities to meet the design requirements. The fibre pattern can be laid in a manner that will tailor the structure to efficiently sustain the applied loads..
- It is easier to achieve smooth aerodynamic profiles for drag reduction. Complex double-curvature parts with a smooth surface finish can be made in one manufacturing operation.
- Composites are dimensionally stable i.e. they have low thermal conductivity and low coefficient of thermal expansion. Composite materials can be tailored to comply with a broad range of thermal expansion design requirements and to minimise thermal stresses.
- Manufacture and assembly are simplified because of part integration (joint/fastener reduction) thereby reducing cost.
- The improved weather ability of composites in a marine environment as well as their corrosion resistance and durability reduce the down time for maintenance.
- Close tolerances can be achieved without machining.

- Excellent heat sink properties of composites, especially Carbon-Carbon, combined with their lightweight have extended their use for aircraft brakes.
- Improved friction and wear properties.

The above advantages translate not only into airplane, but also into common implements and equipment such as a graphite racquet that has inherent damping, and causes less fatigue and pain to the user.

1.9 OBJECTIVE OF STUDY

The purpose of the present work was to synthesize copper-carbon composites and to determine the various physical, mechanical and electrical properties. The main stages of the present work may be written as:

I. Characterization of raw materials (coal tar pitch) with respect to softening point, coking value, ash content, etc.
II. Preparation of carbonaceous green coke material from heat treatment of coal tar pitch.
III. Synthesis of Cu-C material using copper powder and green coke powder by powder technique.
IV. Coating of copper nano particles on the surface of green coke powder through electroless method.
V. Development of carbon monolith and Cu-C composites from the green coke and Cu-C mixed powder and nano copper coated green coke by moulding into plates (45x15x5 mm^3) followed by heat treatment at 1000°C and higher upto 1400°C in inert atmosphere.
VI. Characterization of developed Cu-C composites for:
    - Green and baked bulk density
    - Weight loss (%), volume shrinkage (%), linear shrinkage (%)
    - Electrical resistivity
    - Bending strength
    - Phase analysis by X-ray diffraction (XRD)
    - Surface morphology from scanning electron microscopy (SEM), etc.

CHAPTER 2

COPPER-CARBON COMPOSITE

2.1 INTRODUCTION

Copper-carbon composite is the type of composite in which copper is reinforced in carbon matrix by mixing or coating. As mentioned in chapter 1 composite constitute two or more component, here copper and carbon are two components. There are several methods of preparation of Cu-C composite, in the present work two methods has been used one is powder method and second is electroless coating. An introduction of both carbon and copper are given as following:

2.2 CARBON

Carbon is a chemical element with symbol C and atomic number 6. There are several allotropes of carbon of which the best known are graphite, diamond, and amorphous carbon. Newer allotropes of carbon namely fullerene and carbon nanotube are also discovered in the last three decades. The physical properties of carbon vary widely with the allotropic form. For example, diamond is highly transparent, while graphite is opaque and black. Diamond is among the hardest materials known, while graphite is soft enough to form a streak on paper. Diamond has a very low electrical conductivity, while graphite is a very good conductor. Under normal conditions, diamond has the highest thermal conductivity of all known materials. All the allotropic forms are solids under normal conditions but graphite is the most thermodynamically stable.

All forms of carbon are highly stable, requiring high temperature to react even with oxygen. The most common oxidation state of carbon in inorganic compounds is +4, while +2 is found in carbon monoxide and other transition metal carbonyl complexes. The largest sources of inorganic carbon are limestone's, dolomites and carbon dioxide, but significant quantities occur in organic deposits of coal, peat, oil and methane clathrates. Carbon forms more compounds than any other element, with almost ten million pure organic compounds described to date, which in turn are a tiny fraction of such compounds that are theoretically possible under standard conditions.

Carbon compounds form the basis of all life on earth and the carbon-nitrogen cycle provides some of the energy produced by the sun and other stars. Although it forms an extraordinary variety of compounds, most forms of carbon are comparatively unreactive under normal conditions. At standard temperature and pressure, it resists all but the strongest oxidizers. It does not react with sulfuric acid, hydrochloric acid, chlorine or any alkalis.

At elevated temperatures carbon reacts with oxygen to form carbon oxides, and will reduce such metal oxides as iron oxide to the metal. This exothermic reaction is used in the iron and steel industry to control the carbon content of steel:

$$Fe_3O_4 + 4C_{(s)} \rightarrow 3Fe_{(s)} + 4CO_{(g)}$$

Salient features of carbon (in Graphite form):-

- Light weight, density (1.5 – 2.0 g cm^{-3})
- Good thermal and electrical conductivity

- Withstands high temperatures upto ~ 3000°C (in non-oxidizing atmospheres)
- Improves in strength at elevated temperatures upto ~ 2500°C
- Low coefficient of thermal expansion
- High thermal shock resistance
- Low coefficient of friction
- Inert to most chemicals
- Non-wetting to most molten metals & alloys
- Ability to be tailored to have wide range of properties
- Corrosion and erosion resistant

2.2.1 Allotropes of carbon

The different forms or allotropes of carbon include the hardest naturally occurring substance, diamond, and also one of the softest known substances, graphite buckyballs, carbon nanotubes etc. are given in Figure-2.1

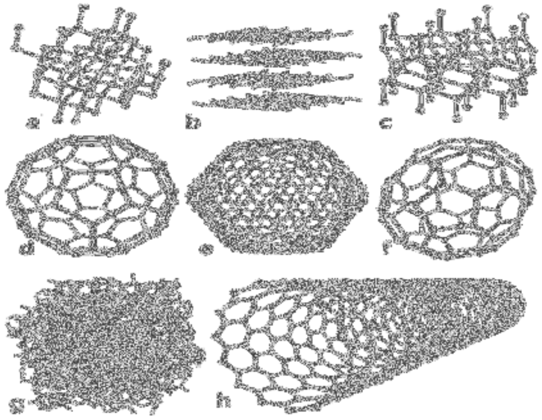


Figure 2.1: Allotropes of carbon: a) diamond; b) graphite; c) lonsdaleite; d–f) fullerenes (C60, C540, C70); g) amorphous carbon; h) carbon nanotube

(a) Diamond

Diamond is the allotrope of carbon where the carbon atoms are arranged in an isometric-hexoctahedral crystal lattice. After graphite, diamond is the second most stable form of carbon. Its hardness and high dispersion of light make it useful for industrial applications and jewelry. It is the hardest known naturally occurring mineral. It is possible to treat regular diamonds under a combination of high pressure and high temperature to produce diamonds that are harder than the diamonds used in hardness gauges.

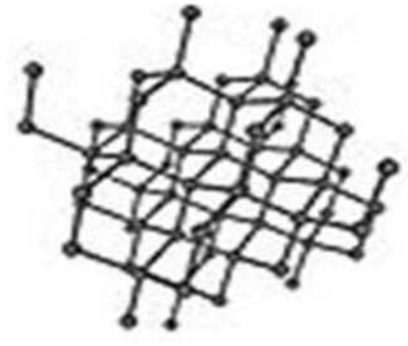


Figure 2.2: Carbon atoms are arranged in an isometric-tetrahedral crystal lattice.

Diamonds are specifically renowned as a material with superlative physical qualities; they make excellent abrasives because they can be scratched only by other diamonds, borazon, ultra hard fullerite, rhenium diboride, or aggregated diamond Nanorods, which also means they hold a polish extremely well and retain their luster.

(b) Graphite

The mineral graphite is one of the allotropes of carbon. Graphite is an electrical conductor, a semimetal, and can be used, for instance, in the electrodes of an arc lamp. Graphite holds the distinction of being the most stable form of carbon under standard conditions. Therefore, it is used in thermo chemistry as the standard state for defining the heat of formation of carbon compounds.

Detailed properties of graphite:

Graphite is a layered compound. In each layer, the carbon atoms are arranged in a hexagonal lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm. The two known forms of graphite, *alpha* (hexagonal) and *beta* (rhombohedral), have very similar physical properties. The alpha form can be converted to the beta form through mechanical treatment and the beta form reverts to the alpha form when it is heated above 1000 °C.

Graphite can conduct electricity due to the vast electron delocalization within the carbon layers. Graphite and graphite powder are valued in industrial applications for its self-lubricating and dry lubricating properties. It is also highly diamagnetic, thus it will float in mid-air above a strong magnet. Graphite forms intercalation compounds with some metals and small molecules. Natural and crystalline graphite's are not often used in pure form as structural materials, due to their shear-planes, brittleness and inconsistent mechanical properties.

Uses of naturally occurring graphite:

Natural graphite are used as refractory, steelmaking, expanded graphite, brake linings, and foundry facings-lubricants

- Graphite Blocks are also used in parts of blast furnace linings where the high thermal conductivity of the graphite is critical.

- Natural graphite is mostly used into carbon rising in molten steel, although it can be used to lubricate the dies used to extrude hot steel.
- It is used for making bipolar plates in fuel cells
- It is also used for making foil in laptop computers keeps them cool
- Natural graphite has uses as the marking material in common pencils, in zinc-carbon batteries, in electric motor brushes, and various specialized applications.

Uses of synthetic graphite:

- As electrodes used in making steel
- Used in batteries and brake linings
- Used in carbon fiber reinforced plastics
- Used as neutron moderator
- Used in radar absorbent materials
- Modern gunpowder is coated in graphite to prevent the buildup of static charge.

(c) Fullerene

Fullerene are a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, or plane. Spherical fullerenes are also called buckyballs, and cylindrical ones are called carbon nanotubes or buckytubes. Graphene is an example of a planar fullerene sheet. Fullerenes are similar in structure to graphite, which is composed of stacked sheets of linked hexagonal rings, but may also contain pentagonal (or sometimes heptagonal) rings that would prevent a sheet from being planar. Figure 2.3 (a),(b)and (c) show different forms of Fullerenes possible.

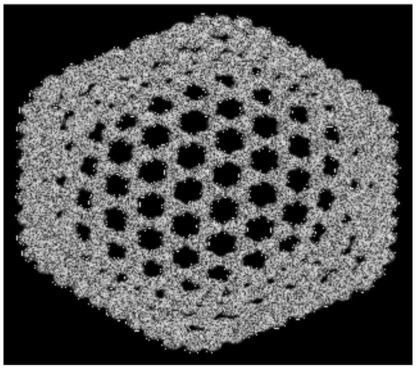


Figure 2.3 (a): The Icosahedral Fullerene C540 electron

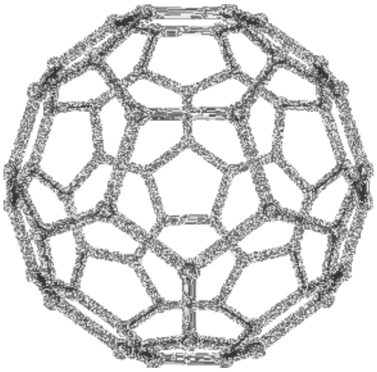


Figure 2.3(b): Buckminsterfullerene C60

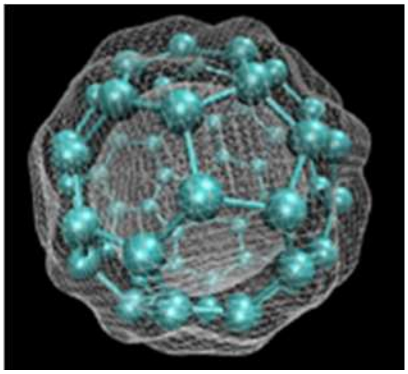


Figure 2.3(c): C_{60} with isosurface of ground state density as calculated with DFT

Fullerenes are sparingly soluble in many solvents. Common solvents for the fullerenes include aromatics, such as toluene, and others like carbon disulphide. Solutions of pure Buckminsterfullerene have a deep purple color. Solutions of C70 are a reddish brown.

After the synthesis of macroscopic amounts of Fullerenes, their physical properties could be investigated. In 1991, it was revealed that potassium-doped fullerenes become superconducting at 18K. This was the highest transition temperature for a molecular superconductor. Since then, Super resistivity has been reported in fullerene doped with various metals as well as potassium.

(d) Carbon Nanotube

Carbon nanotubes are first discovered by Japanese electron microscopiest Sumio Iijima in 1991. Carbon nanotubes also called buckytubes, are cylindrical carbon molecules with novel properties that makes them potentially useful in a wide variety of applications (e.g., nano-electronics, optics, materials applications etc.). They exhibit extraordinary strength, unique electrical properties and are efficient conductors of heat. Inorganic nanotubes have also been synthesized .A nanotube is a member of the fullerene structural family,which also include buckyballs.Whereas buckyballs are spherical in shape, a nanotube is cylindrical , with atleast one end typically capped with a hemisphere of the bucyball structure. Their name is derived from their size since the diameters of the nanotubes are the order of few nanometers, while they can be upto several centimeters in length.

The chemical bonding of carbon nanotube composed of entirely sp^2 bonds, similar to that graphite. This bonding structure is stronger than sp^3 bonds found in diamond, provides the molecules their entire mechanical strength. Carbon nanotubes are mainly two types. These are single walled carbon nanotube and multi-walled carbon nanotubes. Single walled carbon nanotubes are made up rolling down the single graphene sheet as shown in Fig.2.4

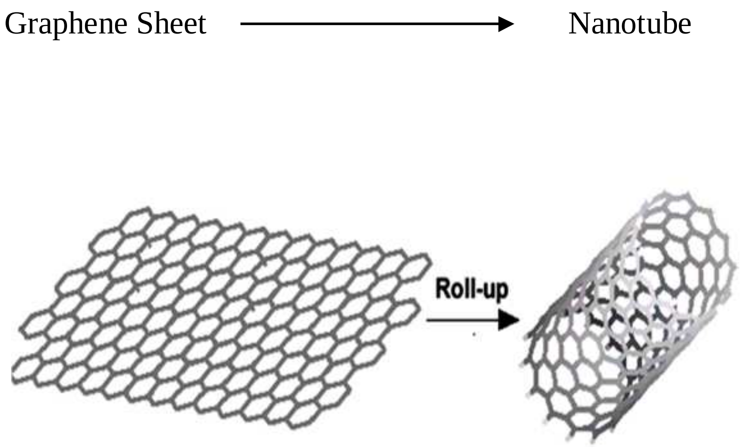


Figure 2.4: Single Walled Carbon Nanotube (SWNT)

One useful application of SWNTs is in the development of the first intramolecular field effect transistors (FETs). The production of the first intramolecular logic gate using SWNT FETs has recently become possible as well. Multi-walled nanotubes (MWNT) consist of multiple layers of graphite rolled in on themselves to form a tube shape. The special place of double-walled carbon nanotubes (DWNT) must be emphasized here because they combine very similar morphology and properties as compared to SWNT, while improving significantly their resistance to chemicals. This is especially important when fictionalization is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT.

Determining the toxicity of carbon nanotubes has been one of the most pressing questions in Nanotechnology. Nanotubes can cross the membrane barriers and suggests that if raw materials reach the organs they can induce harmful effects as inflammatory and fibrotic reactions.

2.2.2 Forms of carbon employed in the present study

(a) Coal Tar Pitch

Coal tar is a principal liquid product resulting from the carbonization of coal, *i.e.*, the heating of coal in the absence of air, at temperatures ranging from about 900° to 1,200° C (1,650° to 2,200°F). Many commercially important compounds are derived from coal tar. In the chemical-process industries, the black or dark brown residue obtained by distilling coal tar, wood tar, fats, fatty acids, or fatty oils is called pitch. Coal tar pitch is a black or dark-brown amorphous residue produced by the distillation or heat treatment of coal tar. It is a soft to hard and brittle substance containing chiefly aromatic resinous compounds along with aromatic and other hydrocarbons and their derivatives; it is used chiefly as road tar, in waterproofing roofs and other structures, and to make electrodes. It is a solid at room temperature and exhibits a broad softening range instead of a defined melting temperature.

Coal Tar pitch is a semi baked form of coke which acts as a binder as well as a source of carbon. It is a pure form of carbon developed by distillation of coal tar and on heating loses about 10-12% of its weight due to moisture loss. It acts as a precursor for the development of green coke. The properties of pitch are defined by parameters like softening point, toluene insolubility, quinoline insolubility, specific gravity and coking value. It is prepared in various combinations of these properties by varying the conditions during preparation. The GC precursor pitch is not available commercially and is synthesized at the National Physical Laboratory in various combinations of the above mentioned properties.

(b) Green coke

Green coke (raw coke) is the primary solid carbonization product from high boiling hydrocarbon fractions obtained at temperatures below 900 K. It contains a fraction of matter that can be released as volatiles during subsequent heat treatment at temperatures up to approximately 1600 K. This mass fraction, the so-called volatile matter, is in the case of green coke between 4 and 15 wt.%, but it depends also on the heating rate. The term raw coke is an equivalent term to green coke although it is now less frequently used. The so-called volatile matter of green coke depends on temperature and time of cooking, but also on the method for its determination.

2.3 COPPER

Copper is a chemical element with the symbol Cu (from Latin: cuprum) and atomic number 29. It is a ductile metal with very high thermal and electrical conductivity. Pure copper is soft and malleable; an exposed surface has a reddish-orange tarnish. It is used as a conductor of heat and electricity, a building material, and a constituent of various metal alloys.

The metal and its alloys have been used for thousands of years. In the Roman era, copper was principally mined on Cyprus, hence the origin of the name of the metal as cyprium (metal of Cyprus), later shortened to cuprum. Its compounds are commonly encountered as copper (II) salts, which often impart blue or green colors to minerals such as turquoise and have been widely used historically as pigments. Architectural structures built with copper corrode to give green verdigris (or patina). Decorative art prominently features copper, both by itself and as part of pigments.

Copper (II) ions are water-soluble, where they function at low concentration as bacteriostatic substances, fungicides, and wood preservatives. In sufficient amounts, they are poisonous to higher organisms; at lower concentrations it is an essential trace nutrient to all higher plant and animal life. The main areas where copper is found in animals are tissues, liver, muscle and bone.

2.3.1 Characteristics

Physical

Copper, silver and gold are in group 11 of the periodic table, and they share certain attributes: they have one s-orbital electron on top of a filled d-electron shell and are characterized by high ductility and electrical conductivity. The filled d-shells in these elements do not contribute much to the interatomic interactions, which are dominated by the s-electrons through metallic bonds. Contrary to metals with incomplete d-shells, metallic bonds in copper are lacking a covalent character and are relatively weak. This explains the low hardness and high ductility of single crystals of copper. At the macroscopic scale, introduction of extended defects to the crystal lattice, such as grain boundaries, hinders flow of the material under applied stress thereby increasing its hardness. For his reason, copper is usually supplied in a fine-grained polycrystalline form, which has greater strength than monocrystalline forms.

The low hardness of copper partly explains its high electrical (59.6×106 S/m) and thus also high thermal conductivity, which are the second highest among pure metals at room temperature. This is because the resistivity to electron transport in metals at room temperature mostly originates from scattering of electrons on thermal vibrations of the lattice, which are relatively weak for a soft metal. The maximum permissible current density of copper in open air is approximately 3.1×106 A/m2 of cross-sectional area, above which it begins to heat excessively. As with other metals, if copper is placed against another metal, galvanic corrosion will occur.

Together with osmium (bluish), caesium (yellow) and gold (yellow), copper is one of only four elemental metals with a natural color other than gray or silver. Pure copper is orange-red and acquires a reddish tarnish when exposed to air. The characteristic color of copper results from the electronic transitions between the filled 3d and half-empty 4s atomic shells – the energy difference between these shells is such that it corresponds to orange light. The same mechanism accounts for the yellow color of gold.

Chemical

Copper forms a rich variety of compounds with oxidation states +1 and +2, which are often called cuprous and cupric, respectively. It does not react with water, but it slowly reacts with atmospheric oxygen forming a layer of brown-black copper oxide. In contrast to the oxidation of iron by wet air, this oxide layer stops the further, bulk corrosion. A green layer of verdigris (copper carbonate) can often be seen on old copper constructions, such as the Statue of Liberty, the largest copper statue in the world build using repoussé and chasing. Hydrogen sulfides and sulfides react with copper to form various copper sulfides on the surface. In the latter case, the copper corrodes, as is seen when copper is exposed to air containing sulfur compounds. Oxygen-containing ammonia solutions give water-soluble complexes with copper, as do oxygen and hydrochloric acid to form copper chlorides and acidified hydrogen peroxide to form copper(II) salts. Copper(II) chloride and copper comproportionate to form copper(I) chloride

2.3.2 Occurrence

Copper can be found as either native copper or as part of minerals. Native copper is a polycrystal, with the largest single crystals found to date measuring 4.4×3.2×3.2 cm. The largest mass of elemental copper weighed 420 tonnes and was found in 1857 on the Keweenaw Peninsula in Michigan, US. There are many examples of copper-containing minerals: chalcopyrite and chalcocite are copper sulfides, azurite and malachite are copper carbonates and cuprite is a copper oxide. Copper is present in the Earth's crust at a concentration of about 50 parts per million (ppm), and is also synthesised in massive stars.

2.3.3 Production

Most copper is mined or extracted as copper sulfides from large open pit mines in porphyry copper deposits that contain 0.4 to 1.0% copper. Examples include Chuquicamata in Chile, Bingham Canyon Mine in Utah, United States and El Chino Mine in New Mexico, United States. According to the British Geological Survey, in 2005, Chile was the top mine producer of copper with at least one-third world share followed by the United States, Indonesia and Peru. The amount of copper in use is increasing and the quantity available is barely sufficient to allow all countries to reach developed world levels of usage.

Reserves

Copper has been in use at least 10,000 years, but more than 95% of all copper ever mined and smelted has been extracted since 1900. As with many natural resources, the total amount of copper on Earth is vast (around 1014 tons just in the top kilometer of Earth's crust, or about 5 million years worth at the current rate of extraction). However, only a tiny fraction of these reserves is economically viable, given present-day prices and technologies. Various estimates of existing copper reserves available for mining vary from 25 years to 60 years, depending on core assumptions such as the growth rate. Recycling is a major source of copper in the modern world. Because of these and other factors, the future of copper production and supply is the subject of much debate, including the concept of Peak copper, analogue to Peak Oil.

Methods

The concentration of copper in ores averages only 0.6%, and most commercial ores are sulfides, especially chalcopyrite ($CuFeS_2$) and to a lesser extent chalcocite (Cu_2S). These minerals are concentrated from crushed ores to the level of 10–15% copper by froth flotation or bioleaching. Heating this material with silica in flash smelting removes much of the iron as slag. The process exploits the greater ease of converting iron sulfides into its oxides, which in turn react with the silica to form the silicate slag, which floats on top of the heated mass. The resulting copper matte consisting of Cu2S is then roasted to convert all sulfides into oxides.

$2\ Cu_2S + 3\ O_2 \rightarrow 2\ Cu_2O + 2\ SO_2$

The cuprous oxide is converted to blister copper upon heating:

$2\ Cu_2O \rightarrow 4\ Cu + O_2$

This step exploits the relatively easy reduction of copper oxides to copper metal. Natural gas is blown across the blister to remove most of the remaining oxygen and electrorefining is performed on the resulting material to produce pure copper.

$Cu_2+ + 2\ e^- \rightarrow Cu$

2.4 FEATURES OF COPPER-CARBON COMPOSITES

2.4.1 Introduction

Copper-carbon composites are also known as the copper-graphite composites and these are the particulate composite having excellent thermal and electrical conductivity and lubrication for the solid contact and sliding that stem from a synergic composites effect of copper and graphite. They have been used for the sliding components such as the electrical brushes and bearing in there engineering applications. These composites exhibit the unique characteristics of both the components i.e. thermal and electrical conductivity of the copper and low thermal expansion coefficient, lubricating and corrosion resistance properties of the graphite.

Copper-carbon composites also find use in microwave travelling wave tube as multistage depressed collector in place of because carbon has a relatively low secondary electron emission coefficient compared to copper provides an excellent thermal conductivity and coated graphite provide and an extreme hardness and stability to the composites.

However, the wear and the contact processes and the mechanism of the composites under the sliding condition have not been well understood because of their complicated microstructure and non-linear mechanical behavior. To develop the high performance sliding contact bearing and electrical brushes, it may be important to study the microscopic processes and the mechanism of the contact surface deformation of the copper graphite composites.

Originally developed for the aerospace industry, copper-carbon composites have now been recognized to provide an extremely cost effective solution for furnace fixture applications. The unique attributes of copper-carbon composites offer important advantages over both metal and graphite fixtures.

2.4.2 Features

1. **Negligible thermal deformation:** Unlike metal fixtures, which twist and wrap over time, Cu-C composites remain flat and actually increase in strength at elevated temperatures. You reduce scrap and maintain tighter part tolerance.

2. **Low thermal mass:** The high strength to weight ratio and low specific heat of Cu-C composite allow to load more parts in each furnace and reduce the cycle time.

3. Excellent Fracture Resistance: Cracks do not propagate catastrophically as it occurs with moulded graphite fixtures.

Some of the most important and useful properties of carbon composite are light weight, high strength at high temperature (3000^{o} C) in non-oxidizing state atmospheres, low coefficient of thermal expansion, high thermal resistivity (higher than that of copper and silver), high thermal shock resistance and low recession in high pressure ablation environments. The mechanical strength of Cu/C increases with temperature, in contrast to the strength of metal and ceramics, which decreases with increasing temperature. These extraordinary properties of Cu-C composites have made these materials extremely useful right for aerospace and defence applications such as brake discs, rocket nozzles, leading edges of re-entry vehicles, furnace heating, thermal management components in space vehicles etc. to those for common man as biomedical implants, glass and high temperature glass and ceramic industry etc. A well-known example for the practical applications of Cu/C composites is in the American Space shuttle, wherein the fuselage nose and the leading edge of the wings are manufactured from Cu/C composites and have withstood a total of 100 missions under the extreme re-entry condition. A national programme has been launched in India for indigenous development of Cu-C composite and related technologies. These composites have been successfully developed and used as nose-tip for the Agni missile and as brake pads for LCA.

CHAPTER 3

EQUIPMENT USED AND CHARACTERISATION TECHNIQUES USED

3.1 EQUIPMENT USED

3.1.1 Ball Mill:

Ball mill, a type of grinder, is a cylindrical device used in grinding (or mixing) materials like ores, chemicals, ceramic raw materials and paints. Ball mills rotate around a horizontal axis, partially filled with the material to be ground plus the grinding medium. Large to medium-sized ball mills are mechanically rotated on their axis, but small ones normally consist of a cylindrical capped container that sits on two drive shafts (pulleys and belts are used to transmit rotary motion).

High-quality ball mills are potentially expensive and can grind mixture particles to as small as 0.0001 mm, enormously increasing surface area and reaction rates. The grinding works on principle of critical speed. The critical speed can be understood as that speed after which the steel balls (which are responsible for the grinding of particles) start rotating along the direction of the cylindrical device; thus causing no further grinding.

Figure 3.1: Ball Mill machine

Following are the specifications for the Ball milling process employed during the work:

Material of balls & jar	Tungsten Carbide
Speed of Base plate	250 rpm
Speed of rotation of Jars	2.5 X (Speed of Base plate) = 625 rpm
Duration of on cycle	30minutes
Duration of off Cycle	5 minutes
Total Ball Milling time	5 hrs.

3.1.2. Electric Furnace

Furnaces range in size from small units of approximately one ton capacity (used in foundries for producing cast iron products) up to about 400 ton units used for secondary steelmaking. Arc furnaces used in research laboratories and by dentists may have a capacity of only a few dozen grams. Electric arc furnace temperatures can be up to 1,800 degrees Celsius. Arc furnaces differ from induction furnaces in that the charge material is directly exposed to the electric arc, and the current in the furnace terminals passes through the charged material.

Figure 3.2: Electric Furnace machine

3.1.3. Instron Universal Bending Strength Testing Machine

The Instron universal testing machine, model 4411, was used to determine the bending strength of the carbonized plates. The test specimen is kept on two knife edges to hold the specimen tightly. A slowly increasing load is applied on the specimen at a cross-head speed of 0.5mm/min through the middle knife edge till the specimen breaks. Stresses so developed in the test are measured with the help of a load cell and recorded on a chart. The vertical movement of the chart corresponds to the deflection in the specimen. Thus, a load versus deflection plot of the specimen is obtained. The bending strength is then calculated as follows:

Figure 3.3: Bending Strength Instron universal testing machine

Bending strength = $(3 P_{max} \times S)/(2bt^2)$

Where, P_{max} = maximum load at which the test-specimen breaks

S = Span length (usually 20 mm)

b = width of the test-specimen

t = thickness of the test-specimen

<u>Body</u>: - The front of the alloy steel U-shaped body has a center cavity with integral wedges which taper toward the open end. The back of body has two angled slots.

Two screws hold a recessed side plate which overlaps each body wedge and grip face. Two steel pins hold the face retainer springs on the front and back of the body.

The closed end of the body has a threaded strut with a machine bore. A control nut threads on the stud and a spindle passes through the bore. An anti-rotation pin passes through the body and sits in the control mechanism spindle slot.

Control Mechanism: - The control mechanism consists of a control nut and a spindle. The control nut threads onto the body stud and has two horizontal handles. The thin spindle end passes through the control nut to the body cavity.

A screw attaches a bearing plate to the spindle end. An anti-rotating pin passes through a vertical slot in the spindle shaft. The spindle shank has a horizontal bore through which a clevis pin passes. A control nut retainer pin passes through a smaller horizontal bore at the spindle center. A check nut attaches to the external threads between the two horizontal bores.

Faces: - A pair of tool steel, wedge shaped grip faces rest on the body’s internal wedges. Two posts on each face attach springs to the body. There is a series of serrations cut into the side of the face which contacts the specimen. Faces may be flat for flat specimens or vee shaped for round specimens, with different grades of serrations.

Faces with other contact surfaces are also available, including rubber coated or surfalloy. An optional specimen centering device attaches to one of the grip faces.

Specimen Centering Device: - The optional specimen centering device is a small metal block with two screws attach to outside of the grip face. A knurled thumb screw secures a thin L-shaped arm which extends outward across the face.

3.1.4 Moulding Machine

Figure 3.4: Pressure Molding Machine

The preparation of the plates of the carbon based composites is carried out using the machine shown in Figure 3.4 through the process of cold pressing. Cold pressing, also known as cold sintering, is a metallurgical process for the production of materials with high mechanical properties. It has been established that the lower temperatures of consolidation may provide more possibilities for the utilization of properties of powders obtained by rapid solidification technologies. Opposite to, conventional or hot sintering, that is carried out at relatively high temperatures (T>Tm/2, when Tm is the temperature of the melting point), the term cold sintering indicates dominant influence of pressing pressure at room temperature.

Figure 3.5: Control Panel for the Moulding Machine

The material to be moulded is put in the piston and dye arrangement which is put on the moulding machine and required load is applied. The curing time refers to the time for which load must be applied to the piston. The load may vary from 0-400 kg/cm2 (0-6000 psi).

3.1.5. Electrical Resistivity Testing Machine

Figure 3.6 shows the setup for a Four Probe Electrical Resistivity Measuring Machine. It measures resistivity of solid pellets at room temperature. This instrument is purely based on Ohm’s law.

Ohm's law applies to electrical circuits; it states that the current through a conductor between two points is directly proportional to the potential difference or voltage across the two points, and inversely proportional to the resistance between them.

Figure 3.6: Set up for electrical resistivity measurement

The mathematical equation that describes this relationship is:

$$I = \frac{V}{R}$$

V is the potential difference measured across the sample in units of volts;

I is the current through the sample in units of amperes and

R is the resistance of the sample in units of ohms.

Figure 3.7: Digital display of Voltage and Current through the specimen

In the setup of this four probe electrical resistivity measuring machine, a constant current (0-10 A) is made to pass through the specimen and voltage drop across the specimen is measured using probes. A constant dc voltage supply (0-5 V/10 A) has an inbuilt voltmeter (mV) and an ammeter (A) which displays the potential drop and the current across the specimen digitally.

3.2 Characterisation

3.2.1 Quinoline and Toluene Insoluble (QI & TI)

The desired amount of sample (0.5gm to 1gm) is stirred for about one hour in quinoline / toluene (30 ml) in a 50ml beaker at 75°C to 90°C in water bath. The entire sample is quantitatively transferred into G-4 gooch crucible inserted into a flask attached to a vacuum pump which removes the quinoline / toluene and the residue is washed three times with about 30ml of acetone. The crucible with the residue is removed from the flask of oven dried at 105°C for about one half to one hour and weighed after it has cooled down in a desiccators for about half an hour. This method is also an ASTM procedure D2318 for QI and ASTM-D4072 for TI.

The concentration of QI/TI is calculated by using following equation:-

QI / TI (%) = ((W3-W2)/W1)) x100

Where W1 → weight of the sample

W2 → weight of empty crucible

W3 → weight of crucible with residue.

3.2.2 Softening Point Measurement

The softening point of the pitches is measured by the Mettler Method, as per the ASTM-D-3104 / DIN 51920 specifications. The Mettler Softening Point of a material is defined as the temperature at which a softened sample of the material, taken in a standard softening point sample cup, flows 20mm out of 6.35 mm diameter opening, on slow heating. The Mettler Softening Point Apparatus consists of a Cartridge Assembly comprising a Cup Holder and a Cylindrical Sample Cup with 6.35 mm diameter orifice and a collector sleeve, which is placed in a Measuring Cell (FP 83) surrounded by a small electrically heated cylindrical furnace.

The test material, taken in the sample cup placed over the cup holder in the cartridge assembly, is heated in the Measuring Cell inside the electric furnace at a rate of 2 °C/min. The temperature at which the first drop of the sample obstructs the light beam placed 20 mm apart from the bottom of the sample is detected by a photoelectric sensor kept inside the Measuring Cell, and displayed on the Central Processing Unit (FP 90) of the Mettler Softening Point Apparatus, as the softening point of the test material.

3.2.3 Determination of coking value (CV)

A sample of the binder is vaporized for a specific time at a specified temperature in equipment that limits the oxygen supply. This method indicates the coke forming properties of the binder.

A 20g portion of the sample is crushed to minus 30mesh. Three grams of the prepared sample is weighed out in a tared porcelain crucible on an analytical balance. The crucible is then placed in a quartzed glass reaction vessel having a provision for flowing of oxygen free nitrogen gas. The quartz glass assembly is then placed in an electrical muffle furnace the temperature of which is gradually raised 950ºC at a specified rate and maintained for exactly 30 minutes. The crucible is then cooled to room temperature and weighed again on the analytical balance. From these observation the coking value is calculated as the residue per cent of the sample taken by given formulae.

CV = ((W1-W2)/W1)*100

Where W1- weight of sample at room temperature

W2- weight of sample at 950^0C temperature

3.2.4 Determination of Ash content

A representative portion of the dry sample is reduced to minus 30 mesh.10gof the prepared sample are weighed out in an ignited crucible (porcelain , silica or platinum) on an analytical balance .the crucible is then carefully heated in an electrical muffle furnace to 950 ºC for 30 minutes. When all the carbon has been combusted the crucible is cooled and weighed again. The ignition at 950 ºC is repeated until constant weighed is obtained. From these observations the ash is calculated as the residue percent of the sample taken.

Ash content= ((w1-w2)/w1)*100

Where w1- weight of sample at room temperature

w2- weight of sample at 950^0C temperature

3.2.5 Determination of specific gravity

A fragment weighing 5-20g of the pitch is suspended by a thin nichrome wire from an analytical balance and its weight both in air and in distilled water at a particular temperature is determined. The specific gravity is then calculated from the relationship

Specific gravity = (a) / (a-b)

Where, a and b are the weights of the specimen in air and in distilled water respectively. The specimens could also be prepared by casting in moulds

3.2.6 Determination of weight loss (WL)

The weight loss in a green carbon plates upon carbonization (HTT~ 1000ºC) or 1400ºC HTT is determined by knowing the weight of the green carbon plates in green and after 1000ºC or 1400ºC states. It is given by the following expression:-

Weight loss (%) = [(W-w)/W] x 100

Where, W = weight of the green carbon plates

w = weight of the carbon plates after 1000ºC or 1400ºC

3.2.7 Determination of volume shrinkage (VS)

The Volume shrinkage loss in a green carbon plates upon carbonization (HTT~ 1000ºC) or 1400ºC HTT is determined by knowing the volume of the green carbon plates in green and after 1000ºC or 1400ºC states. It is given by the following expression:-

Volume shrinkage (%) = [(V-v)/V] x 100

Where, V = volume of the green carbon plates

v = volume of the carbon plates after 1000ºC or 1400ºC

3.2.8 Determination of linear shrinkage (LS)

Linear shrinkage in a green carbon plates upon carbonization (HTT~ 1000ºC) or 1400ºC HTT is determined by knowing the length of the green carbon plates in green and after 1000ºC or 1400ºC states. It is given by the following expression:-

Linear shrinkage (%) = [(L-l)/L] x 100

Where, L = length of the green carbon plates

l = length of the carbon plates after 1000ºC or 1400ºC

A specially NPL designed equipment is employed for the measurement of electrical resistivity. This equipment works on the basis

3.2.9 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity.

The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. This is exemplified by the micrograph of pollen shown to the right. A wide range of magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) to more than 500,000 times, about 250 times the magnification limit of the best light microscopes. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

Magnification

Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. Unlike optical and transmission electron microscopes, image magnification in the SEM is not a function of the power of the objective lens. SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen. Provided the electron gun can generate a beam with sufficiently small diameter, a SEM could in principle work entirely without condenser or objective lenses, although it might not be very versatile or achieve very high resolution. In a SEM, as in scanning probe microscopy, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, or the voltage supplied to the x, y deflector plates, and not by objective lens power.

3.2.10 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultrathin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is tens of thousands times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in both physical and biological sciences. TEMs find application in cancer research, virology, materials science as well as pollution, nanotechnology, and semiconductor research.

At smaller magnifications TEM image contrast is due to absorption of electrons in the material, due to the thickness and composition of the material. At higher magnifications complex wave interactions modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use allow for the TEM to observe modulations in chemical identity, crystal orientation, electronic structure and sample induced electron phase shift as well as the regular absorption based imaging.

The first TEM was built by Max Knoll and Ernst Ruska in 1931, with this group developing the first TEM with resolving power greater than that of light in 1933 and the first commercial TEM in 1939.

3.2.11 X-Ray Diffraction

X-ray scattering techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. These techniques are based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy.

Powder X-ray Diffraction (XRD) is one of the primary techniques used by mineralogists and solid state chemists to examine the physico-chemical make-up of unknown solids. This data is represented in a collection of single-phase X-ray powder diffraction patterns for the three most intense D values in the form of tables of interplanar spacings (D), relative intensities (I/I_o), and mineral name.

The XRD technique takes a sample of the material and places a powdered sample in a holder, then the sample is illuminated with x-rays of a fixed wave-length and the intensity of the reflected radiation is recorded using a goniometer. This data is then analyzed for the reflection angle to calculate the inter-atomic spacing (D value in Angstrom units - 10^{-8} cm). The intensity(I) is measured to discriminate (using I ratios) the various D spacings and the results are to identify possible matches.

Powder XRD (X-ray Diffraction) is perhaps the most widely used x-ray diffraction technique for characterizing materials. As the name suggests, the sample is usually in a powdery form, consisting of fine grains of single crystalline material to be studied. The technique is used also widely for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials).

The term 'powder' really means that the crystalline domains are randomly oriented in the sample. Therefore when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various d spacings in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. For example, the diffraction lines of graphite would be different from diamond even though they both are made of carbon atoms. This phase identification is important because the material properties are highly dependent on structure (just think of graphite and diamond).

Powder diffraction data can be collected using either transmission or reflection geometry, as shown below. Because the particles in the powder sample are randomly oriented, these two methods will yield the same data.

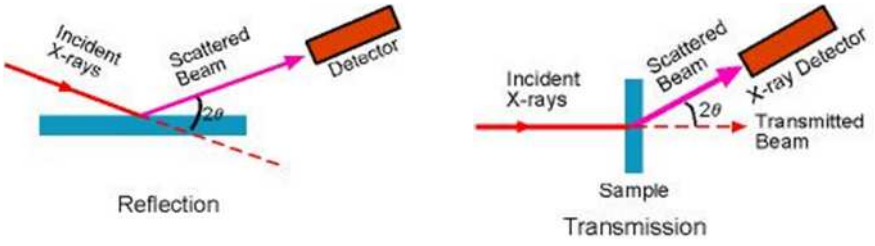


Figure 3.8: Powder X-Ray Diffraction

CHAPTER 4

EXPERIMENTAL WORK

Copper-carbon composites have been prepared by two methods. Here are two approaches as follows:

4.1 APPROACH – I: POWDER TECHNIQUE (MIXING METHOD)

There are several methods available in literature for the development of copper-carbon composites using expensive equipments, viz, by impregnating a carbon substrate with a molten copper or its alloy, by hot isostatic pressing technique or by high frequency induction heating at high pressure. But powder techniques offer the possibilities of producing uniform quality composites with relatively low machining costs. The lack of wettability between copper and graphite (carbon) during the composite processing has been reported to be improved by coating the graphite or carbon fiber with copper using electroless coating before consolidation. This has resulted in the improvement of copper-graphite (or carbon fiber) interface thereby leading to enhancement in the properties of the composite.

Queipo et al reported the use of coal tar pitch binder due to their low cost, easy availability and good wetting behavior during the processing of copper-carbon composites. This coating with pitch was done to study the influence of thermal treatment of coal tar pitch with graphite (synthetic and natural) at a temperature of 420 ^{0}C for 1 hour in nitrogen atmosphere on the interface formed when mixed with copper with a purpose of getting improved properties of copper-carbon composites. It was observed that the flexural and electrical properties of copper-carbon composite (using treated natural graphite) were improved to 39-46 MPa and 0.2-0.7 m cm respectively compared to values of 29-36 MPa and 0.93 mΩcm for carbon composites but without the inherent ductile properties of the copper in the resulting composites.

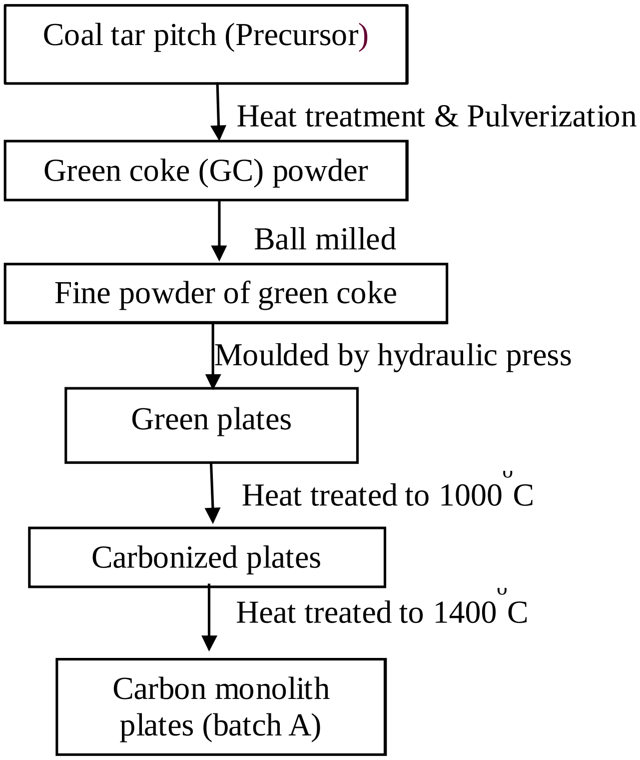


Figure 4.1(a): Powder Method for Green Coke

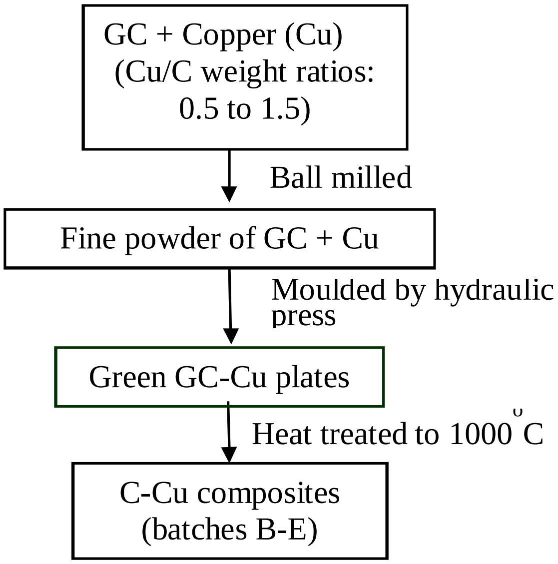


Figure 4.1(b): Powder Method for Cu-C composite

4.1.1 DEVELOPMENT OF GREEN COKE POWDER AND CARBON MONOLITH (BATCH A)

A special commercial available QI free coal tar pitch (CTP) procured from Konark Tar Products Ltd. India was characterized and subjected to heat treatment (HTT) of 500^{o} C to obtain the so called green coke (also called raw coke), which is used as carbon source in this study. The green coke thus prepared was then ground into a fine powder using planetary ball mill at 250 rpm for 5 hours. The powder was characterized and moulded into rectangular plates of size 45x15x15 mm^{3} using a conventional hydraulic press at a pressure 200MPa. These green plates were carbonized at 1000^{o} C followed by employing a heating rate of 20^{o} C/hr upto 250^{o} C and 10^{o} C/hr from 250^{o} C to 1000^{o} C followed by heat treatment (HT) upto 1400^{o} C at the heating rate of 100^{o} C/hr upto 1000^{o} C and 15^{o} C/hr from 1000^{o} C to 1400^{o} C in nitrogen atmosphere to obtain carbon monolith plates (BATCH A). Detailed methodology has been given in fig. 4.1 (a).

4.1.2 DEVELOPMENT OF Cu-C COMPOSITES (BATCH B TO E)

Four batches (B to E) of Cu-C composites were developed from the green coke (GC) powder and electrolytic grade copper powder (Across Organics, 99% pure) varying the Cu/C weight ratio of 0.50, 1.0, 1.3 and 1.5. The various GC-Cu mixture were ball milled in a planetary ball mill for about 5 hours at 250 rpm which were oven dried for 1 hour, moulded into rectangular plates of 45x15x15 mm^3 using hydraulic press at the pressure of 200 MPa. The moulded plates were heat treated at different temperatures (1000^o C or higher upto 1400^o C) in nitrogen atmosphere as mentioned above to get Cu-C composite batches B to E. Step by step methodology has been presented in fig. 4.1 (b).

4.1.3 CHARACTERIZATION

The precursor coal tar pitch and GC powder were characterized with respect to various parameters such as quinolone insoluble (QI), toluene insoluble (TI), softening point, specific gravity, coking value (CV) and volatile matter. The carbon and hydrogen contents as well as C/H ratio were determined using Euro Vector Elemental Analyzer. Weighed quantity of coal tar pitch (CTP), GC and powdered mixtures of Cu-C composites were heat treated in nitrogen from 300 to 1000^o C in steps at the rate 200o C/hr to determine residue mass upon heat treatment (Thermogravimetric analysis, TGA). Carbon monolith batch A derived from the moulded green coke powder and Cu-C composites (batches B to E) were characterized with respect to bulk density, weight loss and volume shrinkage after the heat treatment at 1000^o C and higher upto 1400^o C. The bending strength and electrical resistivity of the carbon monolith after treatment to 1400^o C were also measured by three point bending test using Instron Universal Testing

Machine (model 4411) and by using a laboratory developed four probe apparatus respectively. The bending strength, electrical resistivity and shore hardness of the Cu-C composites were determined after they were heat treated at 1000^o C and 1100^o C. Some representative samples were characterized by X-ray diffraction analysis by employing D-8 Advanced Bruker Powder X-ray diffractmeter using CuKα radiation (λ=1.5418 A) and scanning electron microscopy (LED-440 and ZEISS-EVO MA10).

4.1.4 RESULTS AND DISCUSSION

4.1.4.1 CHARACTERISTICS OF RAW MATERIALS

The characteristics of the precursor coal tar pitch and the green coke powder are given in table 4.1. The coal tar pitch was observed to have low softening point of 86.6^o C and specific gravity of 1.27. It can be seen from the values that precursor coal tar pitch possessed a QI content of 0.2 %, TI content of 22.6 % and CV of 43.8 % which are lower as compared to those of green coke (GC) powder which showed QI of 97 %, TI of 99 % and CV 91 %. This increase in QI, TI and CV of GC powder is attributed to removal of volatile matter on pyrolysis of precursor CTP at the temperature upto 500^o C during GC preparation and also to the dehydrogenative condensation and polymerization reaction between various molecular species of the coal tar pitch. This observation is also supported by the weight change observed in thermal analysis study given in fig. 4.2 which shows sharp decrease in weight of residue of coal tar pitch upto 500^o C beyond which the weight loss decreases very slowly upto 1000^o C. In comparison it is seen that GC powder shows a gradual and low weight loss from a value of nearly 100 % at 300^o C to 92 % at 1000^o C. This is further confirmed by the decreasing hydrogen content from a value of 4.77 % for coal tar pitch to 2.68 % for GC powder (Table-4.1) and increasing

C/H atomic ratio value from 1.61 to 2.82 for coal tar pitch and GC powder there from respectively.

Table 4.1: Characteristics of precursor coal tar pitch and green coke powder

S. No.	Characteristics	Precursor Coal Tar Pitch	Green Coke
1.	Softening Point (^{o}C)	86.6	-
2.	Specific Gravity	1.27	-
3.	Quinoline Insoluble Content (%)	0.2	97
4.	Toluene Insoluble Content (%)	22.6	99
5.	Coking Yield (%)	43.8	91
6.	Volatile Matter	56.2	8.2
7.	B-Resin	22	2
8.	Carbon (%) Hydrogen (%) Atomic C/H Ratio	92.39 4.77 1.61	91.35 2.68 2.82

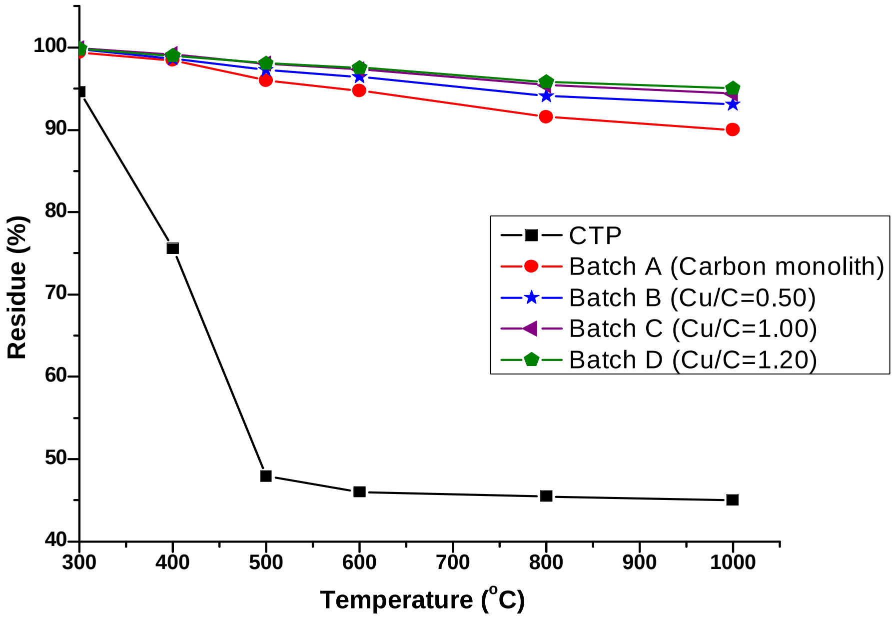


Figure 4.2: Thermal analysis for coal tar pitch (CTP) and Cu-C composites batches A, B, C and D

4.1.4.2 CHARACTERISTICS OF COAL TAR PITCH BASED CARBON MONOLITH (BATCH A)

The characteristics of the carbon monolith batch A developed using GC powder are given in Table 4.2. It is observed that the green carbon monolith (without sintering) possessed a bulk density of 1.3 g/cc at room temperature which increases upto 1.65 g/cc and finally to 1.80 g/cc after the HTT at 1000^o C and 1100^o C respectively. This increase in bulk density is due to removal of volatile matter and subsequent condensation of polyaromatic hydrocarbon resulting in the high volume shrinkage of 27.5 % for the green coke plates with a weight loss of 8.6 % on heat treatment to 1000^o C which is also seen from the thermal analysis shown in fig. 4.1 The electrical resistivity of the carbon monolith plates decreases from 4.8 to 2.9 mΩcm as the HTT is increased from 1000^o C to 1400^o C which is attributed to the immediate proximity between the carbon particles in the carbon monolith due to the weight loss resulting from removal of residual volatile matter and volume shrinkage undergone by the GC derived carbon monolith upon heat treatment to higher temperature. The characteristics values for the bending strength and shore hardness of the monolithic carbon plates were observed to be having reasonably high values of 79 MPa and 103 respectively after the heat treatment of 1400^o C.

Table 4.2: Characteristics of coal tar pitch based carbon monolith batch A

S. No.	**Characteristics**	**HTT (^{o} C)**	**Batch A**
1.	Bulk Density (g/cc)	RT 1000 1400	1.30 1.65 1.80
2.	Weight Loss (%)	1000 1400	8.6 11.2
3.	Volume Shrinkage (%)	1000 1400	27.5 35.1
4.	Electrical Resistivity (mcm)	1000 1400	4.8 2.9
5.	Bending Strength (MPa)	1100 1400	66 79
6.	Shore Hardness	1100 1400	115 103

4.1.4.3 CHARACTERISTICS OF Cu-C COMPOSITES (BATCHES B TO E)

The characteristics of the Cu-C composites batched developed with GC (batches B to E) are given in the Table 4.3. It seen from the values that then the green density values (before sintering) for Cu-C composites are higher and found to be in the range of 2.10 to 2.95 g/cc for batches B to E having Cu/C weight ratio varying between 0.5 to 1.5 (Table-4.3). This increase in green bulk density is due to the higher density of metallic copper (8.9 g/cc) present in these composites and further the density is expected to increase as the copper content is increased in these composites. It is important to mentioned here that the bulk density of all the composites decreases on further heat treatment at 1400^o C and this is attributed to the loss of copper from the composite plates resulting from the melting and removal of Cu which starts at temperatures above the melting point of Cu i.e. 1083^o C.

The values for the volume shrinkage and weight loss of the composites given in Table-4.3 shows that the volume shrinkage and weight loss increase as HTT is increased upto 1400^o C which due to self sintering property of GC and removal of volatile matter. The volume shrinkage and weight loss however, decreased as the Cu content is increased (batches B to E) which is expected since it is GC component of the composites which shows volume shrinkage and copper does not undergo any volume shrinkage or weight loss on heat treatment.

The electrical resistivity of these composites given in Table-4.3 for batches B to E shows that the electrical resistivity is decreased from a value of 1.53 to 0.66 mΩcm at 1000^o C and 0.79 to 0.58 mΩcm at 1100^o C as copper to carbon content (weight ratio) in the composites is increased from 0.5 to 1.5. This attributed to the self sintering property of GC which increases the proximity among the carbon particles and also to the high conductivity of copper present in Cu-C composites.

It is also seen that bending strength is maximum in composites (batch B) having higher quantity of GC which help in making a dense composite due to the self sintering ability of the GC powder. The bending strength of the composites at 1000^o C is decreased gradually on increasing the Cu/C ratio from 0.5 to 1.5 from a value of 115 MPa for batch B to 69 MPa for batch E and this is due to the decreased quantity of GC or increased quantity of copper in the composites (batches B to E) and also to the lack of wettability between copper and carbon. It is also noticed from the values that the bending strength increases as the HTT increases from 1000° C to 1100° C for batch E while it decreases for batches B, C and D. This observation probably indicates that the limiting Cu/C weight ratio and limiting HTT in these composites are around 1.0 and 1100° C for obtaining composites with better bending strength. .

Table: 4.3: Characteristics of Cu-C composite batches B to E

S. No.	**Characteristics**	**HTT (° C)**	**Composition of Cu-C composite batches (weight percentage) along with Cu/C ratio**			
			B Cu:C (0.5)	**C Cu:C (1.0)**	**D Cu:C (1.3)**	**E Cu:C (1.5)**
1.	Bulk Density (g/cc)	RT 1000 1100 1400	2.10 2.75 2.81 2.63	2.41 3.10 3.17 2.98	2.48 3.19 3.25 3.04	2.95 3.32 3.37 3.03
2.	Weight Loss (%)	1000 1100 1400	5.01 5.32 12.76	4.08 4.25 13.00	3.81 3.94 12.80	3.65 3.58 14.90
3.	Volume Shrinkage (%)	1000 1100 1400	28.18 31.80 43.84	25.90 26.50 39.56	24.58 25.80 37.88	22.50 24.40 35.21
4.	Electrical Resistivity (mΩcm)	1000 1100 1400	1.53 0.79 0.58	1.20 0.89 0.42	0.82 0.68 0.23	0.66 0.58 0.23
5.	Bending Strength (MPa)	1000 1100 1400	115.0 86.2 72.5	92.0 83.1 70.1	87.8 78.0 64.0	69.0 74.5 62.7
6.	Shore Hardness	1000 1100 1400	98 92 77	92 86 71	83 78 67	79 68 59

The shore hardness of these composites decreases for batches B to E from 98 to 79 as copper to carbon ratio increases this is due to softness of copper and also decreases as temperature increases from 1000° C to 1400° C which is again due to the melting/softness of copper.

4.1.4.4 X-RAY ANALYSIS

The X-ray diffraction pattern of Cu-C composites (batch B with Cu/C weight ratio 0.50) heat treated to different temperature from 1000° C to 1400° C are given in fig. 4.3. The X-ray diffraction patterns shows characteristics peaks of copper at 20 = 43.29°, 50.43° and 74.13°. The peak due to carbon is not very prominent since the GC derived carbon at 1000° C to 1400° C is generally turbostatic.

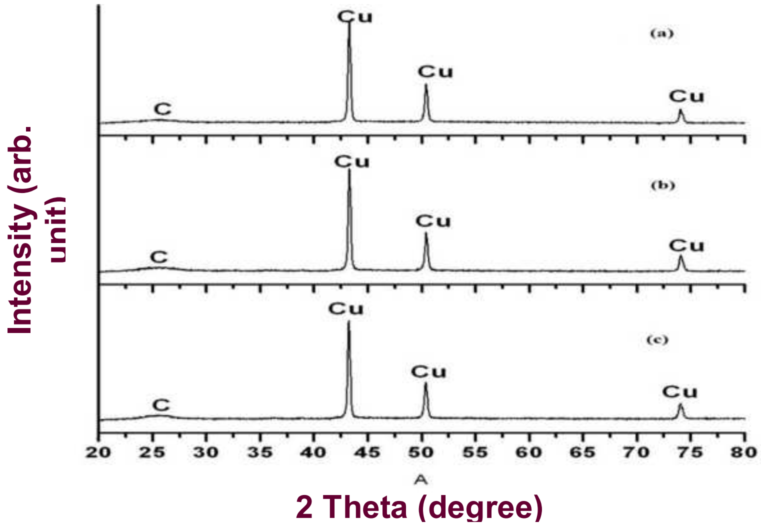


Figure 4.3: X-ray diffraction patterns of Cu-C composite batch B (Cu/C weight ratio = 0.5) heat treated to (a) 1000° C (b) 1100° C (c) 1400° C

4.1.4.5 SEM ANALYSIS

The scanning electron micrographs of the Cu-C composites batch C (Cu/C ratio of 1.0) and batch E (Cu/C ratio of 1.5) heat treated to 1100^{o} C are given in Fig. 4.4 in back scattered mode and Fig. 4.5 in secondary emission mode respectively. The micrographs show that the copper is distributed into the carbon matrix of the composites (heat treated to 1100^{o} C) and no clear interface between copper and carbon is visible in these composites. The SEM studies support our observation mentioned earlier under the subheading characteristics of Cu-C composites that copper is lost through melting at temperature above 1083^{o} C resulting in voids which leads to deterioration in physical, mechanical and electrical properties.

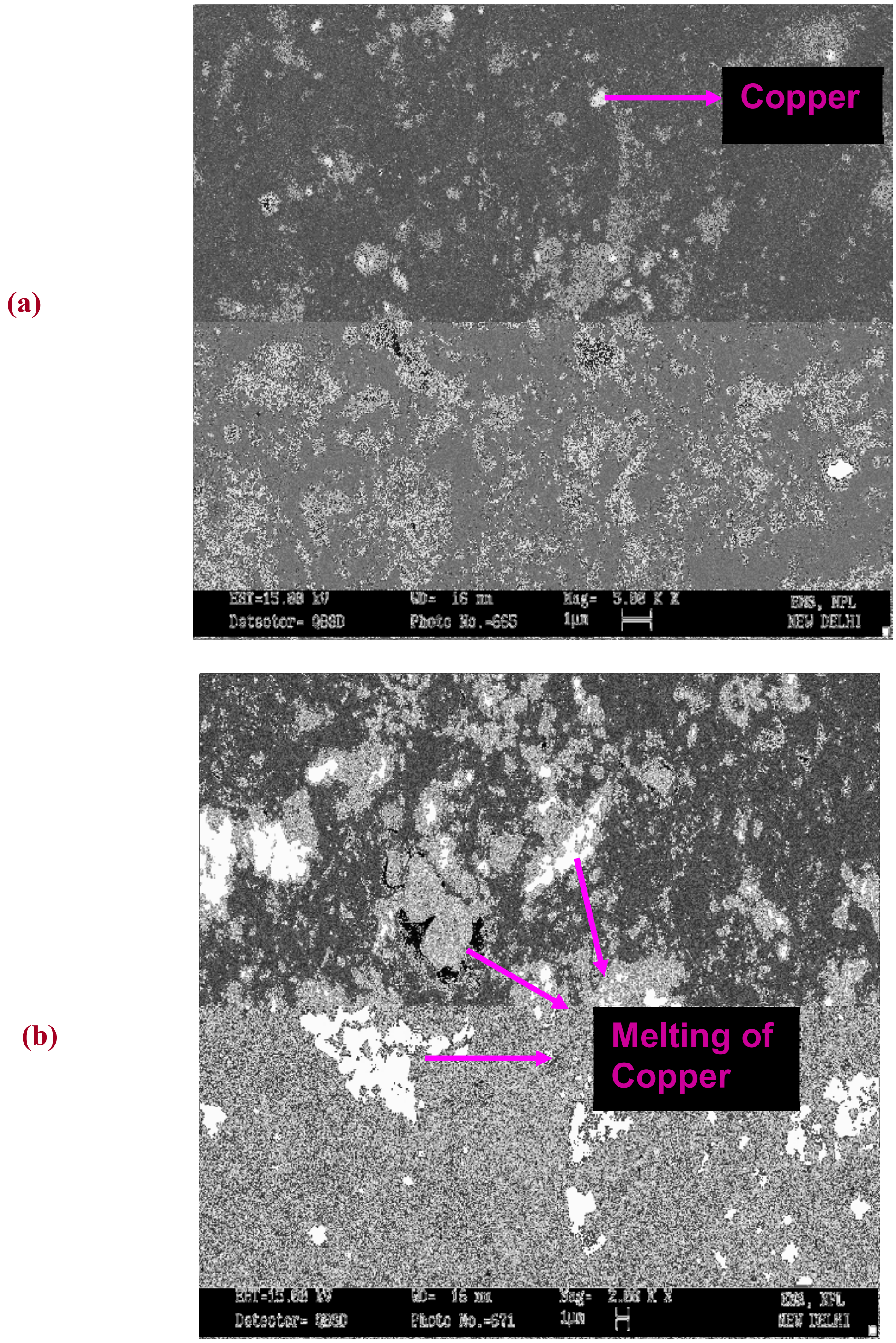


Figure 4.4: Scanning electron micrographs of Cu-C composite batch C (Cu/C weight ratio = 1.0) heat treated to (a) 1100° C and (b) 1400° C

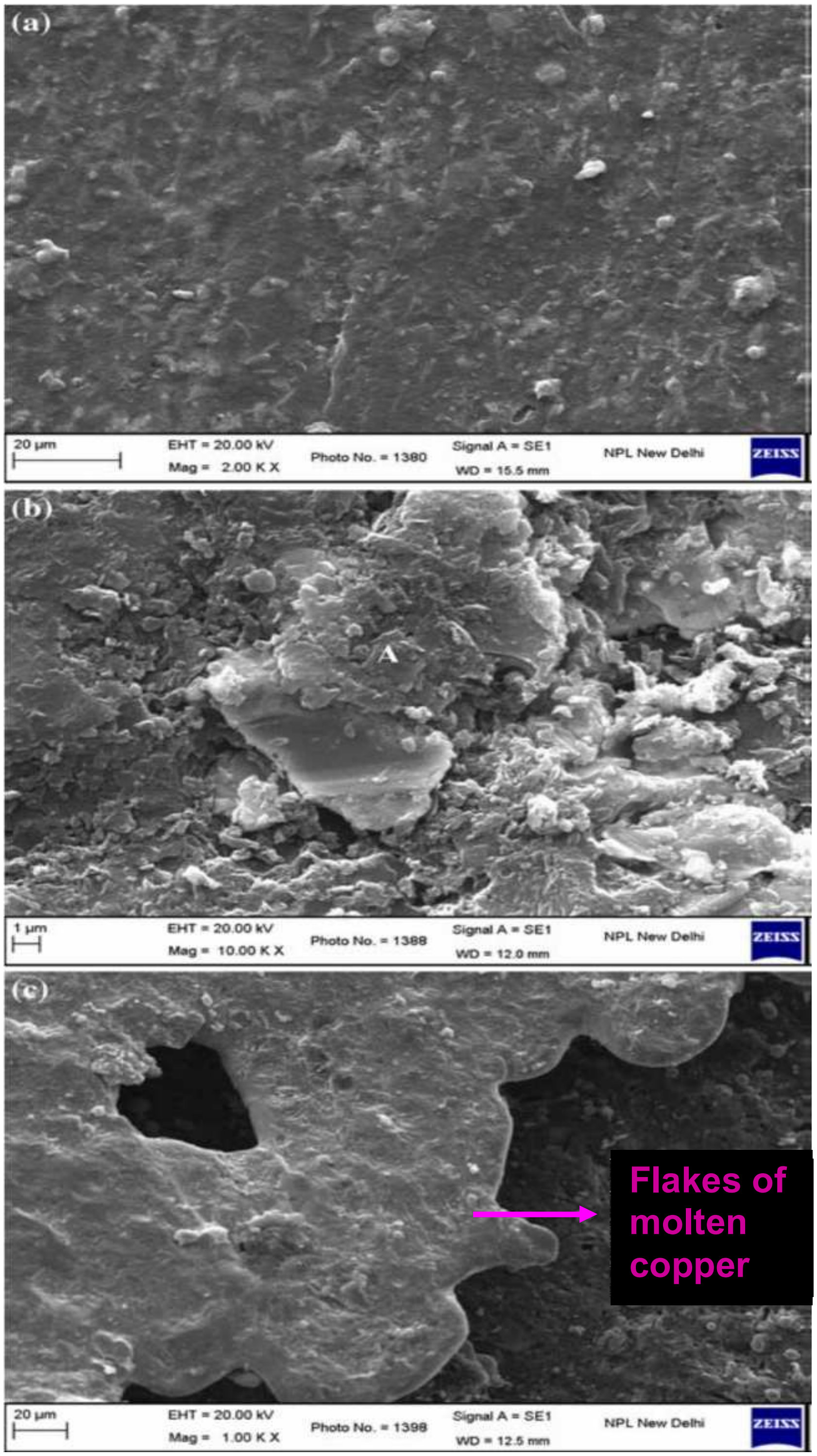


Figure 4.5: Scanning electron micrographs of Cu-C composite batch E (Cu/C weight ratio = 1.5) heat treated to different temperatures (a) 1100^o C (b) 1400^o C (c) fractured surface (1400^o C HTT)

4.2 APPROACH II – ELECTOLESS PLATING

4.2.1 INTRODUCTION

The formation of a continuous metallic film on a surface without the use of an electric current and when done by a definite process is called electroless plating. Electroless plating is defined as the controlled autocatalytic deposition of a continuous film at catalytic interface by the reaction in solution of a metal salt and a chemical reducing agent. This definition excludes such processes as conventional electroplating, which uses externally supplied electrons as the reducing agent; uncontrolled precipitation of metal powders; immersion films produced by displacement reactions, often mistakenly labeled as electroless processes; thermal decomposition films; and the various types of sputtering and evaporation techniques. Electroless deposition can produce films of metals, alloys, compound and composites on both conductive and non-conductive surfaces.

The first description of electroless plating was that of von Liebig in 1835 involving the reduction of silver salts by reducing aldehydes. Progress in this field remained slow, however until world war II. One significant problem was the need for very high purity chemicals, as the surface being plated must maintain autocatalytic activity. Many substances react with and poison the catalyst surface even if present only in trace amounts. Impurities can also cause the opposite problem, over activity. Colloidal material and fine particles can promotes uncontrolled autocatalytic reactions owing to extremely high surface areas. Another reason for the lack of wide interest in electroless plating was cost. Chemical reducing agent are much more expensive than electricity.

The growth of electroless plating is directly traceable to: (1) the discovery that some alloys produced by electroless deposition, notably nickel, phosphorus. Having unique properties; (2) the growth of electronics industry , especially the development of printed circuits; and (3) the large scale introduction of plastics into everyday life.

Modern electroless plating began in 1944 with the rediscovery that hypophosphite could bring about nickel deposition. Subsequent work led to the first patents on commercially usable electroless nickel solutions. Although these solutions were very useful for coating metals, they could not be used on most plastics because the operating temperature was 90-100 C. The first electroless nickel solution capable of wide use on plastics was introduced in 1966. This solution was usable at room temperature and was extremely stable.

Electroless copper solution underwent similar development during the same period. Early printed circuit boards used mechanically attached eyelets to provide electrical conductivity between the copper sheathing laminated on two sides of a plastic board. Electroless copper plating provided a less expensive better conductive path, allowing greater numbers and smaller sizes of holes. Later electroless coppers even replaced the laminated bulk copper sheathing in the semi additive and additive processes. Interest in electroless plating grew as it was shown that uniformity of deposition was very high. Current density complications, customized anodes and special plating fixtures needed for the use of electrolytic plating were eliminated. The lack of requirements for electrical continuity made electroless baths an idea solution to the problem of plating unconnected metal areas on printer circuit boards.

4.2.2 THEORY OF ELECTROLESS PLATING

The theory and practice of electroless plating parallels that of electrolytic plating. The actual metal reduction and film development occurs at the interface of the solution and the item being plated in both the electrolyte and the electroless processes. The main difference is that the electrons in the electroless plating are supplied by a chemical reducing agent present in solution. In electroplating, these electrons are supplied by an external source as a battery or generator. This means that electroless solutions are not thermodynamically stable, because the reducing agent and the metal salt are always present and ready to react.

The simplest electroplating bath consists of solution of a soluble metal salt. Electrons are supplied to the conductive metal surface, where electron transfer to and reduction of the dissolved metal ions occur. Such simple electroplating baths are rarely satisfactory and additives are required to control conductivity, pH, crystal structure, throwing power and other conditions.

Electroless solution contain a metal salt, a reducing agent, a pH adjuster or buffer, a complexing agent, and one or more additives to control stability, film properties, deposition rates, etc.

Most reducing agent are too slow, giving insufficient plating rates, or too fast, resulting in bulk decomposition. Each combination of metals and reducing agents requires a specific pH range and both formulation. The metal salt and the reducing agent must be replenished at periodic intervals. Buffers, complexes and other additives are added to compensate for drag out losses, and to counter bath aging effects such as accumulation. Stabilizers are typically used at a few to a few tens ppm and may affect deposition colour or metal ductility or control spontaneous decomposition reactions.

The ideal electroless solution deposits metal only on an immersed article, never as a film on sides of the tank or as a fine powder. Room temperature electroless nickel baths closely approach this ideal; electroless copper plating is beginning to approach this stability when carefull controlled. Any metal that can be electroplated can theoretically also be deposited by electroless plating. Only a few metals i.e. nickel, copper, gold, palladium, and silver are used on any significant commercial scale.

Electrolytic plating rates are controlled by the current density at the metal – solution interface. The current distribution on a complex part is never uniform, and this can lead to large differences in plating rate and deposit thickness over the part surface. Uniform plating of blind holes, re-entrant cavities and long projections is difficult.

A primary advantage of electroless solutions is the ability to produce conductive metallic films on properly prepared non-conductors, along with the ability to uniform coat any platable object. The most complex geometric shapes received a uniformed plated film. Film thickness range from less than 0.1 micrometer where only conductivity or reflectivity is wanted, to greater than equal to 0.1 millimeter for functional applications.

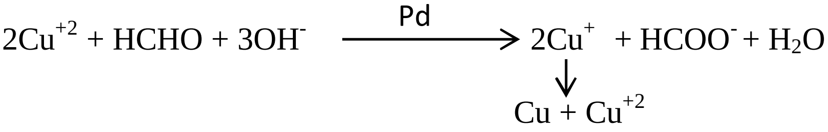
Electroless plating rates are affected by the rate of reduction of the dissolved reducing agent and the dissolved metal ion which diffuse to the catalytic surface of the object being plated. When an initial continuous metal film is depositd, the whole surface is at one potential determine by the mixed potential of the system. The current density is same everywhere on the surface as long as flow and diffusion are unrestricted so the metal deposited is uniform in thickness over the whole surface. However, maximum plating are usually lower for electroless plating. Extremely thin film of electroless coating are not uniform, because the initial deposition is confined to discrete nucleation sites that grow and coalesce into a film.

Mechanism of Electroless Copper Solution:

The electroless copper solution consists of the following reagents:

1. Copper sulfate – source for copper.
2. Formaldehyde - reducing agent.
3. Caustic - basic medium.
4. Chelating agent (amines, gluconates, glucoheptaonates, various EDTAs**,** and tartrates) governs the plating rate and has a marked influence on the properties of the deposit and the bath stability.

As shown in the chemical reaction below, with the presence of pdladium as a catalyst and under a strongly basic medium, electrons are obtained from the reducing agent, formaldehyde, to reduce the cupric ions to metallic copper.



$$2Cu^{+2} + HCHO + 3OH^{-} \xrightarrow{Pd} 2Cu^{+} + HCOO^{-} + H_2O$$

$$2Cu^{+} \downarrow Cu + Cu^{+2}$$

However, the reduction proceeds through a cuprous state. *An* excess of cuprous oxide formation will cause the reduction reaction to proceed out of control. To inhibit the formation of cuprous oxide, air is bubbled slowly through the electroless copper solution and small complexing agents are added to the solution. The presence of these complexing agents turns the electroless copper bath into chelated solution.

4.2.3 Sensitization and Activation of Green Coke Carbaneous Material

Electroless coating of copper in nano-dimension on carbon materials requires surface treatment with $SnCl_2$ and $PdCl_2$. Before coating Green Coke carbon powder prepared in section 4.1.1 from coal tar pitch was sensitized with 0.5 % solution of $SnCl_{2.}$ In this step, dry green coke powder of 8.0 g was poured in a funnel and flask arrangement fitted with filter paper. Then, it was washed with a freshly prepared solution of stannous chloride until the green coke powder gets completely wet with the solution.

The sensitized GC powder was dried for 30 minutes at room temperature. After drying, the powder was washed with distilled water. The sensitized and dried green coke powder was again poured in a similar funnel and flask arrangement fitted with filter paper. Then, it is washed with a freshly prepared 0.001 % solution of palladium chloride until the green coke powder gets completely wet with the solution and is dried for 30 minutes at room temperature.

4.2.4 Preparation of Bath solution

Bath solution was prepared by dissolving 18 g of copper sulphate pentahydrate ($CuSO_{4.}5H_2O$) in 2 litre distilled water. Then potassium sodium tartarate (43 g) was added to this solution which acts as complexing/chelating agent. 20g of sodium hydroxide pellets were also added to maintain the pH of the solution.

The dried activated graphite powder was then added in the prepared bath solution. Also, formaldehyde solution was added into the solution. Formaldehyde acts as a reducing agent. The temperature and pH of the solution were maintained at 70-80^o C anh 11-12 respectively.

The mixture was thoroughly stirred for 8-10 minutes with the help of a magnetic stirrer. Mixing was continued till colour change was observed. Coated green coke was filtered and washed with distilled water and then dried it in an oven at 100^o C for 4-5 hours.

This copper coated green coke powder was again coated with copper through the same above electroless method to obtain double coating of copper on green coke and to increase the copper contents. Since the copper in dimension is more reactive and gets converted into copper oxide during electroless coating. Therefore hydrogenation of single and double coated green coke was carried out at 300^o C in the mixed atmosphere of H_2 and N_2 gas to reduce copper oxide into copper. Detailed methodology has been given in Fig. 4.6

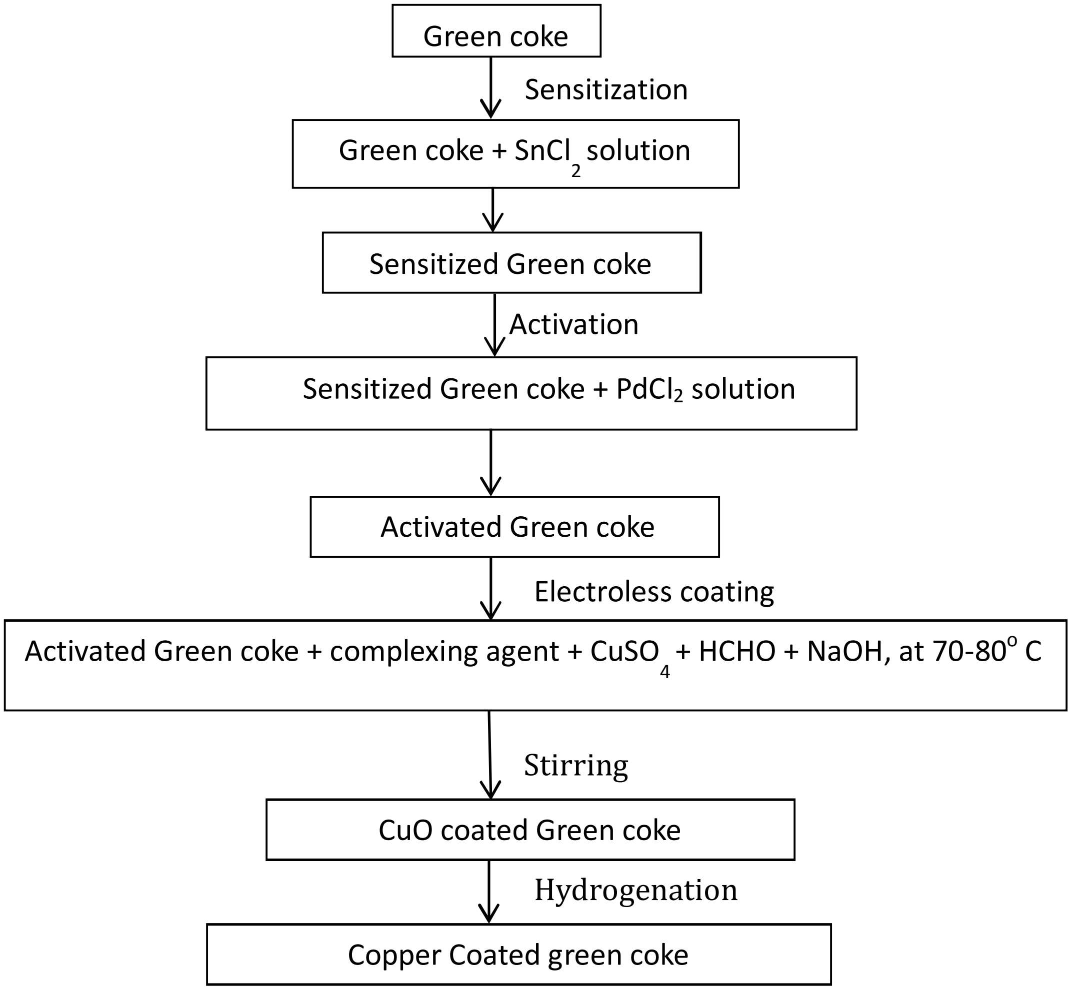


Figure 4.6: Methodology: Electroless coating

4.2.5 DEVELOPMENT OF Cu-C COMPOSITES THROUGH ELECTROLESS (BATCHES F AND G)

Two batches (F and G) of Cu-C composites were prepared from electroless copper coated green coke mentioned above. Batch F was prepared from single layer copper coated green coke powder and batch G from double layer copper coated green coke powder. Cu/C ratio in batches F and G found to be 0.5 and 1.28 respectively by calculation. Coated green coke were moulded into rectangular plates of 45x15x5 mm^3

using hydraulic press at a pressure of 200 MPa. The moulded plates were heat treated at temperature of 1000^o C in nitrogen atmosphere. After that batches F and G were characterized with respect to bulk density, weight loss, volume shrinkage, bending strength, electrical resistivity and shore hardness. Batches were also characterized by XRD, SEM and TEM.

4.3 RESULTS AND DISCUSSION

4.3.1 CHARACTERISTICS OF Cu-C COMPOSIES (BATCHES F AND G)

The characteristics of the Cu-C composites batches F and G are given table 4.4. It seen from the values that the bulk density of green coke based plates (without sintering) is 1.30 g/cc (Table-4.2) and the green density values (before sintering) for Cu-C composites are higher and found to be in the range of 1.90 to 2.65 g/cc for batches F to G having Cu/C weight ratio varying between 0.5 to 1.28 respectively (Table-4.4). This increase in green bulk density is due to the higher density of metallic copper present in these composites and further the density is expected to increase as the copper content is increased in these composites.

The values for the volume shrinkage of the composites at 1000^o C given in Table-4.4 shows that the volume shrinkage decreases as Cu/C weight ratio is increased which is expected since it is GC component of the composites which shows volume shrinkage and copper does not undergo any volume shrinkage or weight loss on heat treatment.

The electrical resistivity of these composites given in Table-4.4 for batches F and G shows that the electrical resistivity is decreased from a value of 0.42 to 0.14 mΩcm at 1000^o C as copper to carbon content (weight ratio) in the composites is increased from

0.5 to 1.28 respectively. This attributed to the high conductivity of copper present in Cu-C composites.

It is also seen that bending strength is more in batch F than batch G having higher quantity of GC which help in making a dense composites due to the self sintering ability of the GC powder. The bending strength of the composites at 1000^{o} C is decreased from a value of 156 MPa for batch F and 110 MPa for batch G and this is due to the decreased quantity of GC or increased quantity of copper in the composites (batches F and G) and also to the lack of wettability between copper and carbon.

The shore hardness of these composites decreases for batches F to G from 97 to 90 as copper to carbon ratio increases this is due to softness of copper.

Table 4.4: Characteristics of Cu-C composite batches prepared by electroless

S. No.	**Characteristics**	**HTT(^{o} C)**	**Cu-C composite with Cu/C ratio**	
			Batch F **Cu:C** **0.50**	**Batch G** **Cu:C** **1.28**
1.	Green Bulk Density (g/cc)	RT	1.90	2.65
2.	Baked Bulk Density (g/cc)	1000	2.90	3.37
3.	Weight Loss (%)	1000	4.94	3.18
4.	Volume Shrinkage (%)	1000	37.63	24.0
5.	Electrical Resistivity (mΩcm)	1000	0.42	0.14
6.	Bending Strength (MPa)	1000	156	110
7.	Shore Hardness	1000	97	90

4.3.2 X-RAY ANALYSIS

The X-ray diffraction pattern of Cu-C composites using D-8 Advanced Bruker Powder X-ray diffractometer (batch F with Cu/C = 0.5) heat treated to at 1000^o C is given in figure 4.8 show major peaks corresponding to copper at 2θ of 43.34, 50.61 and 74.14^o in the green as well as in baked Cu-C composites. XRD pattern show peaks of copper oxides in green composite material before hydrogenation and after hydrogenation these peaks are disappeared confirmed that copper oxide had been completely converted into metallic copper. However, sharp peak due to carbon in Cu coated GC in the green material (without HTT) is not observed and one small peak at 2θ of 26.59° is due to turbostatic carbon at 1000° C.

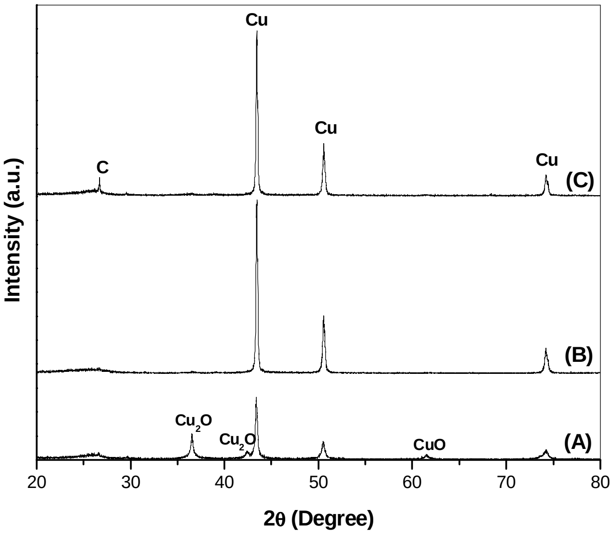


Figure 4.7: XRD patterns for electroless Cu coated GC powder with Cu/C=0.50: (A) green powder before hydrogenation, (B) green powder after hydrogenation and (C) C-Cu baked composite (HTT 1000° C) after hydrogenation.

4.3.3 SEM AND TEM ANALYSIS

The scanning electron micrographs (SEM, ZEISS-EVO MA10) of copper powder obtained through electroless method without heat treatment after hydrogenation given in figure 4.9(A) shows that the flower like structure due to agglomeration of copper particles, while TEM (FEI-TECNAI G2F30 S300kB) image figure 4.9(B) confirmed the agglomeration of copper particles with spherical shape having particle size in the range of 20 to 100 nm. The SEM micrograph in figure 4.8 (A) of carbon monolith exhibit uniform surface with some micropores, while figure 4.8 (B) clearly shows that Cu was deposited on the surface of the GC particles. The surfaces of Cu-C composites of batches F and G heat treated to 1000^{o} C show agglomeration of copper particles at some places figure 4.9 (C), (D) which could be due to the melting and fusion of nanocopper during carbonization upto 1000^{o} C though the melting temperature of bulk copper is 1083^{o} C

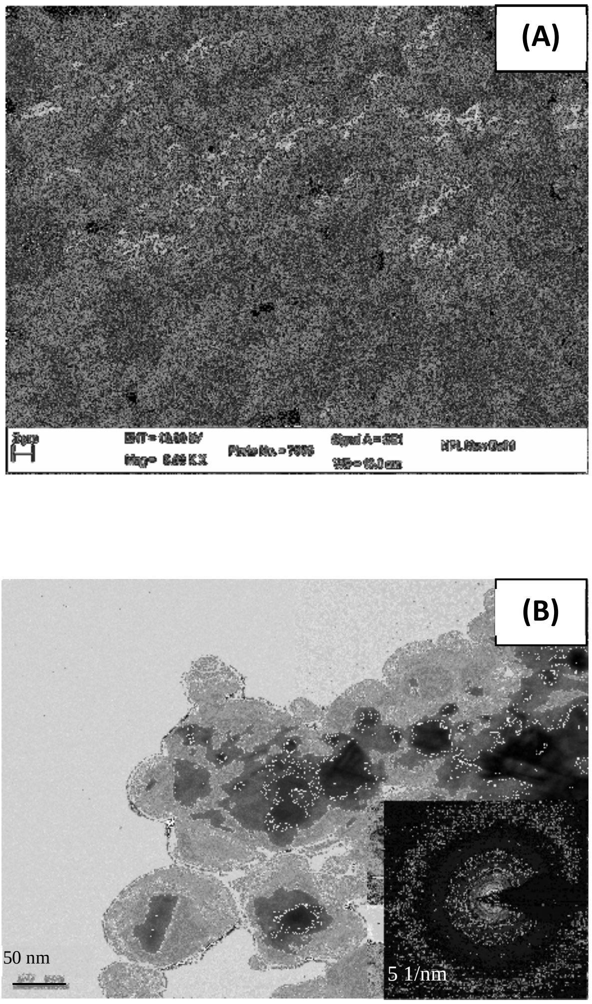


Figure 4.8: SEM (A) and TEM (B) images of metal copper obtained through electroless method after hydrogenation (inset: selected area diffraction pattern (SADP) of polycrystalline copper

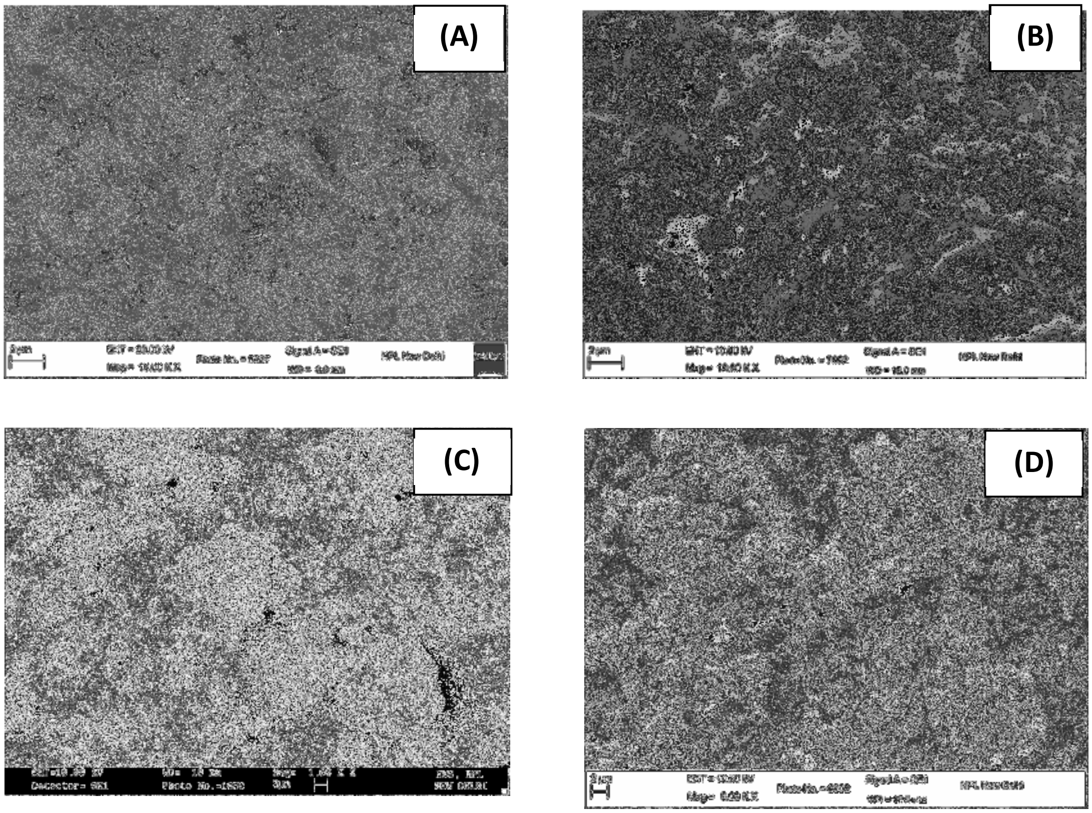


Figure 4.9: SEM images of: (A) carbon monolith - batch A, (B) Cu coated GC (Cu/C=1.28, batch G) green powder, (C) Cu-C baked composite (Cu/C=0.5, batch F) and (D) Cu-C baked composite (Cu/C=1.28, batch G)

CHAPTER 5

CONCLUSION

Properties of any composite depend upon the characteristics of the used raw materials (copper and carbon), method of preparation and heating temperature. Several copper-carbon composites have been developed by varying Cu/C ratio using coal tar pitch based green coke and commercial copper powder by powder method and also from nano copper coated green coke material by electroless method. The composites prepared by powder method, showed better properties such as bulk density of 2.75-3.32 g/cc, bending strength of 115-69 MPa and electrical resistivity from 1.53-0.66 mΩcm depending on the Cu/C ratio varying from 0.50 to 1.5, heat treated at temperature of 1000°C inspite of lack of wettability between carbon and copper. The copper-carbon composites developed using electroless nano copper coated green coke material exhibited significant improvement in bulk density, bending strength and electrical resistivity.

In comparison of both the methods powder and electroless, it is seen that there is no significant difference in the properties like weight loss, volume shrinkage and shore hardness. But bulk density, electrical properties and bending strength are much better in electroless method than powder method at same Cu/C ratio and HTT

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CHAPTER 6

APPLICATIONS

5.1 APPLICATIONS OF COPPER-CARBON COMPOSITES

5.1.1 COPPER OXIDE-GRAPHITE COMPOSITE ELECTROLESS: APPLICATION TO NITRITE SENSING

The concerns over a significant increase in the accumulation of toxic substance in the environment due to human activities have lead to a substantial increase in environmental monitoring in recent years. Therefore, the development of electrode materials for direct amperometric detection of various analytes is growing area of elecroanalytical chemistry. The most commonly used amperometric electrodes are made of carbon based materials. However, these typically suffer from slow electron transfer rates resulting in high over potentials required for oxidation/reduction of different compounds. Recently, special attention has been given to chemically modified carbon electrodes and carbon composite electrodes to improve the electrocatlytic activity for determination of different analytes. Chemically modified elecrodes are mainly prepared by electrochemically depositing catalyst onto carbon electrodes surfaces, while carbon composite elecroless are usually formed by mixing catalysts with carbon powder. Noble metals: platinum, palladium, rhodium, iridium and gold, are well-known oxidation catalysts with high activity and stability and have been succuessfully used incorporated in carbon electrodes. However, due to the high cost of these metals, attention has been given to non noble metal based catalysts, such as transition metal oxides. Copper-based catalysts represent an interesting class and proved to be electrocatlytic active for biosensing of glucose and carbohydrates, saccharides, alditols, amino acids, alcohols and amines, organic compounds, volatile organic compounds, cyanides and nitriles, owing to the excellent electrocatalytic activity of copper oxide towards the oxidation/reduction of these analytes. The environmental impact caused by the build-up of high nitrites concentrations, due to their use as additives in food, fertilizers in agriculture and as corrosion inhibitors, and the problems caused by the contamination of food products, water and environment are significant concerns. Nitrite ion can have damaging effects via two mechanisms. They can combine with blood pigments producing methaheamoglobin in which oxygen is no longer available to the tissues. Also they may interact in the stomach with amines and amides forming highly carciogenic N-nitrosamine compounds. Therefore, nitrite determination is important for environment and for public health. Although nitrites are electroactive at carbon electrodes, their oxidation requires undesirably high overvoltages. As a result, the voltametric determination of nitrite suffers from interference by other readily oxidisable compounds. In order to improve the selectivity of the determination of nitrite, the operating potentials should be efficiently lowered which can be achieved by modifying suitable electrocatalysts on the surface of carbon electrodes.

5.1.2 PREPARATION AND CHARACTERIZATION OF COPPER-ACTIVATED CARBON COMPOSITES ELECTRODES FOR SUPERCAPACITORS

Recently, supercapacitors have been developed as a new type of energy storage device. They are expected to be used in many applications such as the power source or electric vehicles because of their high power density. However, since the energy density of spercapacitors is only several Wh.Kg^{-1} and therefore much lower than that of rechargeable batteries, the capacitance and pseudocapacitance. High surface area carbon materials, such as activated carbon, activated carbon fiber, carbon aerogel, and so on, have been developed to improve the characteristics of the high energy density supercapacitors. Deposition of copper on the activated carbons may provide an economical means of enhancing energy storage of the resulting electrodes via the redox transition of this metal. Carbon composite materials in which the nanometer scale metallic compounds were highly dispersed could be prepared by a dopping method. They were characterized as the electrode for supercapacitors , and the effect of the copper on the BET surface area and pore size distribution of the activated carbons was analyzed. Phenolic resin was were used as the starting material for preparation of activated carbons (AC). The percentage of copper in the raw materials was 2 wt% .

The advantage of the capacitances of these capacitors series can be attributed to the presence of copper, which assisted the storage of the energy.

5.1.3 NEW COPPER –CARBON COMPOSITE MATERIAL APPLIIED IN RAIL-TYPE LAUNCHING SYSTEM

During the operation of a rail-type electromagnetic launching system, the state of the sliding friction between armature and rail, friction drag, contact resistance etc., directly affect the system operation and performance. Copper-carbon composite material can be used on the parts of the armature which contacts the rails. It should not only provide good conductivity , but lubrication, as well; thus, the performance is improved material preparation and composite material moulding crafts. It is possible to make a composite material in which a 3-D metal net is obtained: something that can not be obtained by conventional copper-graphite powder metallurgy or by metal impregnation. Graphite particles are distributed uniformly within the net, improving abrasion resistance and voltage drop over common copper-carbon composite material. The static test showed that this new type of composite material has better electrical performance than former brush material in the same conditions, and the dynamic tests showed that the temperature rise is not big when the brush with this new composite material is switched on with big current and the surface abrasion is smaller during sliding. The good conductivity and sliding contact performance are important for application in electromagnetic launching systems.

5.1.4 HIGH ELECTRICAL CONDUCTIVITY ENGINEERING APPLICATION

Intercalation compounds of graphite of the acceptor type have potential engineering applications because of their attractive electrical conductivity properties. The first approach concerns a composite, formed by enclosing an intercalation compound synthesized from high quality crystalline in a matrix of copper. With this form of composite it is found that there are both intrinsic and extrinsic advantages pertaining to the use of a material that has a conductivity higher than and a density lower than that of copper. The second form is a composite compound of intercalated graphite fibers contained in a matrix of epoxy. Extraordinary advantages in this case result from the fact that while intercalation of the fibers produces an order of magnitude increase in their electrical conductivity is increased by two orders of magnitude over its pristine fiber counterpart. It is projected that these desirable electrical conductivity characteristics portend large scale uses for for the acceptors compounds of graphite as substitutes for the present standard conductors, and as a way of upgrading the performance of carbon/graphite materials.

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