CHAPTER VI

INVESTIGATIONS ON APPLICATIONS OF GLASS-LIKE CARBON

6.1. INTRODUCTION

It has already been shown in Chapter I that glass-like carbon is a new material as it combines some of the properties of glass such as lusture, mode of fracture and imperviousness with those of normal industrial carbons. Its chief characteristics such as high strength and hardness, high resistance to corrosion and erosion, low porosity and permeability make glass-like carbon a versatile material in a wide range of analytical, metallurgical, mechanical, electrical, electronics and biomedical applications(1-13). Further, it has also been mentioned that the manufacturing technology of this form of carbon has been kept highly secretive and consequently there are only few firms in the world with no one in India producing these carbons. It has been shown in Chapters III-V that glass-like carbons can be developed by the controlled carbonization upto a temperature of 950 °C or higher of a suitable phenol formaldehyde resin precursor. The characteristics of glass-like carbons made in the present investigations have been found to compare well with those available commercially(14,15).

The present chapter describes the development and applications of glass-like carbon in biomedical, semiconductor, analytical and other specialised fields. It has been demonstrated over the past two decades that carbon in all its forms including the glass-like form is uniquely
biocompatible with living tissues\(^{5-7,16-21}\) and is now universally accepted by the surgeons for implantation in the body. Several publications point out the use of glass-like carbon or vitreous carbon for heart valve, dental implants and percutaneous connections in the body\(^{5-7,22,23}\).

The glass-like carbon dental implants have been designed and developed for the first time in India and subjected to clinical tests and subsequently to field trials on Rhesus monkeys and finally on human beings for replacing damaged teeth, in collaboration with the Military Dental Centre, Army Hospital, Delhi. The development and results of these biomedical investigations have been discussed in detail in this chapter.

The applications of glass-like carbons in semiconductor, analytical and other specialised fields namely thin film deposition, have also been examined. Accordingly, glass-like carbon cylindrical crucibles of different capacities ranging from 6 to 85 ml as well as small conical crucibles of 20 to 50 ml capacities and boats with around 10 ml capacity have been made. Besides this, resistor plates of size about 48 mm x 16 mm x 2.4 mm with a slot of size 28 mm x 8 mm x 1.2 mm have also been made for the thin film applications.

6.2. DEVELOPMENT OF GLASS-LIKE CARBON DENTAL IMPLANTS

Glass-like carbon dental implants provide an important application in the biomedical field. As this form of carbon is non-porous, bacteria cannot be entrapped. This carbon is
also not degraded in oral fluids. Owing to its hardness, no abrasion can occur. The glass-like carbons are compatible with soft tissues and bone(24-26). Their presence produces no inflammatory response, no foreign body reactions, no systemic responses in the major organs, tissues, blood and urine.

The physical properties of this carbon are comparable to those of natural dentine (tooth). Because of the excellent clinical history, standardised artefacts of glass-like carbon are manufactured by the Vitredent Corporation, Los Angeles (presently the company has changed its name), specifically for endosseous implantation by dental surgeons(7).

Grenoble and Voss(27) demonstrated the successful implantation of glass-like carbon to replace teeth, and showed that glass-like carbon is superior to most of the other materials for this particular application in which the implant protrudes through surface tissues. The tissues can grow so close to the surface of the glass-like carbon (unlike in metals) that the ingress of infection into the jaw is prevented. These tissues were also found to grow into crevices (groove areas) cut into specimens to ensure strong fixation. It is not fully established whether or not the tissues actually bond to the carbon surface. Meffert(28) has, however, shown that carbon is active in promoting new tissue growth.

6.2.1. DESIGN AND DEVELOPMENT OF DENTAL IMPLANTS

In the present investigations glass-like carbon tooth root implant has been designed which is close to that used by Lemons et al(29) and reported in the literature(6,30). The
design of the implant is shown in Fig. 6.1. This implant has built-in crevices (annular grooves) to increase the surface area to have sufficient tissue growth for better retention and a hole through the main axis to allow a gold post and polymethyl methacrylate (PMMA) crown to be fitted.

A Resole grade of phenol formaldehyde resin was prepared by reacting phenol and formaldehyde in a molar ratio of 1.5 in the presence of ammonia catalyst (2% by weight of phenol). Resin was brought to the viscous stage and was then transferred to 10-12 mm diameter glass tubes and subsequently cured in hot air oven at 70°C till solidification. The solidified resin tubes were turned on a lathe machine using silicon carbide tip tools as per design shown in Fig. 6.1. The resin implants were cured upto 150-200°C and then carbonized in an inert atmosphere of ultra high purity nitrogen in an electrically heated muffle furnace to a temperature of 1000°C at controlled rates of heating. These carbonised implants were heat-treated to 1800-2000°C in a graphite tube furnace. The change in dimensions and other characteristics of glass-like carbon dental implants in the process of development are shown in Table 6.1.

6.2.2. FIELD TRIALS OF DENTAL IMPLANTS ON ANIMALS AND HUMAN-BEINGS

The glass-like carbon dental implants prepared in these investigations were subjected to clinical tests and then field trials on Rhesus monkeys at the Animal Experiment Unit of the All India Institute of Medical Sciences, New Delhi, and
All dimensions in mm.

Fig.6.1. GLASS-LIKE CARBON DENTAL IMPLANT.
<table>
<thead>
<tr>
<th>CHARACTERISTIC</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green Water Immersion Density ( (g \ cm^{-3}) )</td>
<td>1.24-1.29</td>
</tr>
<tr>
<td>Baked Water Immersion Density ( (g \ cm^{-3}) )</td>
<td>1.44-1.55</td>
</tr>
<tr>
<td>Carbonization Yield (%)</td>
<td>67-70</td>
</tr>
<tr>
<td>Length (mm)</td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>22-24</td>
</tr>
<tr>
<td>Carbonized</td>
<td>18-20</td>
</tr>
<tr>
<td>Linear Shrinkage (%)</td>
<td>16-18</td>
</tr>
<tr>
<td>Maximum Diameter (mm)</td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>8.5-8.6</td>
</tr>
<tr>
<td>Carbonized</td>
<td>7.0-7.1</td>
</tr>
<tr>
<td>Shrinkage Along the Maximum Diameter (%)</td>
<td>17-18</td>
</tr>
<tr>
<td>Hole Diameter (mm)</td>
<td></td>
</tr>
<tr>
<td>Green</td>
<td>1.95-2.05</td>
</tr>
<tr>
<td>Carbonized</td>
<td>1.5-1.6</td>
</tr>
<tr>
<td>Shrinkage Along the Hole Diameter (%)</td>
<td>20-25</td>
</tr>
<tr>
<td>Transverse Breaking Strength (MPa)</td>
<td>255-290</td>
</tr>
<tr>
<td>Shore Hardness</td>
<td>90-105</td>
</tr>
</tbody>
</table>
The glass-like carbon dental implants prepared in the present investigations were subjected to field trials on three Rhesus monkeys after steam sterilisation. Out of three monkeys, two were sacrificed after 123 and 147 days of the implantation. Just prior to sacrifice, the implants mobility was evaluated and rated according to the lateral displacement (mm) of the implant from its vertical axis. The gingival sulcus was probed buccally and lingually and pocket depth recorded in mm. The similar recordings were made on the third animal after ten months. These observations on the three animals are shown in Table 6.2. It was found that the mobility of the implant on the third animal was almost nil showing thereby very good bio-compatibility between the body tissues and the glass-like carbon implant. Further the animal was alive and well after 22 months of the implantation.

Forty healthy persons, free from any infection and systemic diseases, e.g., diabetes, mallitus, cardiovascular diseases etc. were selected between the age of 18 to 40 years. These cases required extraction of single root (tooth) in upper anterior arch. Pre-extraction X-ray was done to rule out any type of bone loss in respect of concerned tooth. This X-ray was used as a guide also to modify the shape of carbon implant. Carbon implants were sterilized under steam pressure prior to insertion.

Extraction was carried out under asceptic condition and the socket was left untouched, if the root implant, root of
### TABLE 6.2

RESULTS OF FIELD TRIALS ON ANIMALS

<table>
<thead>
<tr>
<th>Rhesus Monkey</th>
<th>No. of days before sacrifice</th>
<th>Time between extraction and implantation</th>
<th>Mobility (m.m.)</th>
<th>Gingival sulcus (m.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>123 days</td>
<td>Immediate</td>
<td>0.75</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>147 days</td>
<td>do-</td>
<td>0.50</td>
<td>1.5</td>
</tr>
<tr>
<td>3</td>
<td>Alive, splint removed</td>
<td>do-</td>
<td>0.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
the tooth, matched in shape and size. If any difference in socket size and shape was observed, it was modified to the size and shape, to the requirement, using a sterile diamond stone.

The implant was embedded in the socket leaving the stump portion projecting out. The socket edges were closed by putting one suture mesial and second suture distal to the implant. The implant was further immobilized with figure "8" wire splint to each of immediate neighboring tooth.

Patients were administered 5,00,000 I.U. streptopencillin per day I/M (AST) for the first seven days following the implantation. Sutures were removed after seven days and it was checked that the implant is not under any occlusal load. Patients were seen every fortnightly. Clinical evaluation was carried out for 12 weeks. Wire splints were removed after 12 weeks. An acrylic jacket crown (complete) was fabricated using readymade dowels. These dowel crowns were cemented over the implant stump in the conventional manner.

A typical case in which glass-like carbon dental implant is being fixed on to human-being after removal of damaged tooth is shown in Fig.6.2. The crown being fixed onto the glass-like carbon dental implant is shown in Fig.6.3 and the final appearance after the dental implantation is shown in Fig.6.4.
Fig. 6.2. Glass-like carbon dental implant being fixed after removal of damaged tooth.
Fig. 6.3. Crown being fixed on to the glass-like carbon dental implant.
Fig. 6.4. **FINAL APPEARANCE AFTER THE DENTAL IMPLANTATION**
6.2.3. FIELD TRIAL RESULTS OF DENTAL IMPLANTS

It was observed that gingival sulcus depth and mobility of implants decreased with time. Out of forty cases only two implants failed because of dehiscence and were pulled out after one and a half month of the insertion. This failure was mainly due to the wrong selection of case with inadequate bulk (Labio palatal thickness) of bone. Further, the breakage and fracture in use was not there and the rejection mobility and inflammatory response was nil (cf. Table 6.3).

Periodical clinical evaluation was carried out for a period of 12 to 18 months. These field trial experiments have shown a very good acceptability of these implants by the body tissues and the fixation of these implants due to growth of tissues around them and the continuous use of implanted tooth in the human body without any problems. All these observations show indirectly a very good biocompatibility of these dental implants with the human body. The indigenous knowledge developed during the present investigations will be passed on to other dental centres in the country.

6.3. GLASS-LIKE CARBON ARTEFACTS FOR ANALYTICAL APPLICATIONS

6.3.1. GLASS-LIKE CARBON CRUCIBLES FOR SILICON PROCESSING

Besides the use of glass-like carbon dental implants, efforts were made in the present studies to use glass-like carbon crucibles in silicon processing application for solar energy utilization. Solar grade silicon is melted in special graphite crucibles at 1450 C and allowed to recrystallize in the process of cooling it. The graphite crucibles has to be
**TABLE 6.3**

RESULTS OF FIELD TRIALS ON HUMAN-BEINGS

<table>
<thead>
<tr>
<th>No. of Cases</th>
<th>Breakage/ Fracture in use</th>
<th>Duration of follow-up</th>
<th>Acceptance</th>
<th>Rejection of Systemic Local causes (Dehiscence)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>Nil</td>
<td>12-18 months</td>
<td>38</td>
<td>Nil</td>
</tr>
</tbody>
</table>


of certain strict specifications in respect of density, strength, thermal expansion and purity. Such graphite crucibles are not commercially produced in the country and have to be imported at premium prices. It was therefore proposed to develop glass-like carbon crucibles since they meet the above mentioned characteristics.

Attempts were made in the present studies to make glass-like carbon crucibles of I.D. 16-45 mm, height 24-53 mm and wall thickness of about 2.5 mm having capacities ranging from 6 ml to 85 ml, from the phenol formaldehyde resins by three different methods. First method involved the use of hot pressing in suitably designed die-steel dies as shown in Fig.6.5. Shrinkage problems were faced in the case of crucibles of capacity 10 to 30 ml during the process of hot pressing and these problems became severe when large diameter crucibles possessing capacity of 100 to 150 ml were made. As a result, the hot pressing technique was abandoned since the crucibles could not be successfully removed from the moulds without breakage.

In the second method, the phenol formaldehyde resin was solidified in beakers of capacity 50 to 250 ml which were subsequently machined to make resin crucibles of I.D. 20-55 mm, height 30-65 mm and with wall thickness of about 3 mm of various capacities ranging from 10 to 150 ml capacity. The third method involved the use of a mixture of phenol formaldehyde and catechol formaldehyde resins taken in the ratio of 4:1 with a view to improve the apparent density of
Fig. 6-5. Hot pressing semi-positive mould for making phenol formaldehyde resin crucible.
the crucibles at the green and baked stages both. The mixed resin was casted in suitably designed moulds having thin coating of high temperature paraffin wax for easy removal of semi-cured resin crucibles from the moulds. The semi-cured crucibles prepared from the second and third methods were cured upto 200°C in hot air oven. The water immersion densities of cured crucibles by the second and third method were found to be in the ranges of 1.13 - 1.18 and 1.23 - 1.28 g cm$^{-3}$ respectively. These crucibles were subsequently carbonized in nitrogen atmosphere to 950°C in an electrically heated muffle furnace. The carbonized crucibles were then heat-treated to 2000°C and above in a graphite tube furnace. The heat-treated crucibles possessed a water immersion density of 1.45 to 1.55 g cm$^{-3}$ and a fractured surface resembling glass.

The crucibles were used for melting and crystallization of solar grade silicon. It has been found that these crucibles work successfully without any breakage which usually occurs during the solidification of molten silicon. It can be concluded from the present investigations that glass-like carbon crucibles can serve well in silicon processing for solar energy utilization.

6.3.2. GLASS-LIKE CARBON RESISTOR PLATES AND CRUCIBLES FOR THIN FILM APPLICATIONS

Glass-like carbon artefacts have potential applications in the field of thin films, where this material can be used either as resistor plates of high current capacity or as crucibles. The test material is taken on the resistor plate or in the crucible and is made to evaporate under conditions
of high temperature and high vacuum to result in the deposition of thin films on suitable substrates.

Glass-like carbon resistor plates of size about 40 mm x 16 mm x 2.4 mm with a rectangular slot of size 28 mm x 8 mm x 1.2 mm (for containing the test material) have been made by hot pressing of phenol formaldehyde resin on a hydraulic press which are cured upto 200 C and then carbonized to 1000 C. The plates so obtained possess all the characteristics as those of the NPL made glass-like carbon mentioned in chapter III.

The plates are further heat-treated to 2500 C by the procedures already described in chapter II. The heat-treated resistor plates have been given a field trial in the actual set up for depositing thin films of aluminium and have been found to work very well. Extensive trials are, however, in progress and it is expected that glass-like carbon resistor plates can serve as a potential material in the thin film applications for replacing the conventional costly materials like tungsten, molybdenum and titanium.

The glass-like carbon crucibles of I.D. 15 mm, height 20 mm with a wall thickness of about 2 mm prepared in a similar fashion as described earlier in the chapter can be used as containers for keeping aluminium discs over which high density electron beam is impinged in order to evaporate the metal for deposition of thin films on suitable substrates. It is hoped that these crucibles on field trial will be superior to the conventional ceramic materials like aluminia, because of their better ceramic behaviour such as temperature bearing.
6.3.3. GLASS-LIKE CARBON ARTEFACTS FOR OTHER APPLICATIONS

The technology for making glass-like carbon has been developed in the course of present investigations and glass-like carbon artefacts in various shapes such as crucibles, boats, plates, slotted plates, rods, dental implants and discs have been made. A photograph of these artefacts is depicted in Fig.6.6. It is intended to exploit various other applications like in Fuel Cells of this newer material in the future.
Fig. 6.6. GLASS-LIKE CARBON ARTEFACTS FOR VARIOUS APPLICATIONS
REFERENCES

4. S. Yamada, DCIC report 68-2, April 1968, Battelle Memorial Institute, Ohio, USA.