Study and characterization of bio-active glass coating composite with and without hydroxyapatite on titanium and SS316L to regenerate supporting bony growth to established better bonding and stability

Tarak Das¹, Pratik Das² and Piyali Basak²

¹ Dept, of Biomedical Engineering, Netaji Subhash Engineering College, Garia, Kolkata
² School of Bioscience and Engineering, Jadavpur University, Kolkata

ABSTRACT

Over a period of time a number of biomaterials have been developed and are used for hard tissue and joint. Metal Biomaterials gained its importance in recent time for having advantageous mechanical properties, nontoxic behavior, and biocompatibility. But one of the main drawbacks of using metallic implants is that they are bio-inert and inside the body they become encapsulated by dense fibrous tissue. This impedes proper stress distribution at the implant bone interface, which can result in an interfacial failure and loosening of the implant and finally lead to crack or fracture in the adjacent bone. Bone cement (Poly Methyl Methacrylate) can be used to improve the implant fixation but it becomes brittle with time so it gets loosen from the surface as well as it has a poor solvent resistance. Calcium Phosphates, specially Hydroxy-Apatite \([\text{Ca}_10(\text{PO}_4)_6(\text{OH})_2]\) have been widely used as coating materials on metallic implants due to the bio-active nature. Plasma-spray technique, in particular, has been widely investigated by many researchers and has been proposed as a reasonable coating method. But during the plasma spraying process, high flame temperature is required which can lead to compositional changes and structural transformation of Hydroxy Apatite (HA). So, after this procedure the uniformity of physical and chemical properties as well as bio-activity of Hydroxy Apatite (HA) could be lost. In this study one bio glass composition was prepared by matching its thermal expansion coefficient nearer to thermal expansion coefficient of metallic substrate specially Titanium and SS-316L. The metallic substrate coated with this Bio glass with and without mixing with HA with a certain percentage. The coating adherence property was studied by 3-point bending moment and bioactivity studied by using Simulated Body fluid which showed very promising result. The coating was also characterized with analysis of DTA-TGA, Surface reflectance also Surface Roughness.

Keywords: Hydroxy Apatite, SS-316L, Glass Coating, 3 point Bending-Moment, DTA-TGA, Surface Reflectance, Surface Roughness.

*Corresponding E-mail: tarakdas111@gmail.com
1. INTRODUCTION

During last few decade there have been developed of several bioactive coating materials[1] by different techniques for using orthopedical implants to increase better bonding and stability. Calcium Phosphates, specially Hydroxy apatite [Ca_{10}(PO_{4})_{6}(OH)_{2}] have been widely used as coating materials on metallic implants due to its bio-active nature to facilitate bonding with bone.

Plasma-spray technique, in particular, has been widely investigated by many researchers and has been proposed as a reasonable coating method. But during the plasma spraying process, high flame temperature is required which may lead to compositional changes and structural transformation of Hydroxy apatite (HA). So, after this procedure the uniformity of physical and chemical properties as well as bio-activity of Hydroxy apatite (HA) could be lost. Most implants today are made from either titanium-based alloys or alloys made from a mix of cobalt and chromium. Both possess excellent mechanical properties but neither is able to bond with bone. As a result, these metals rub against the bones into which they’ve been implanted, creating wear and tear that shortens implant lifetimes. In many research works bone cement (Poly methyl methacrylate) have been used for better bonding and stability but it may result in deterioration of the adjacent bone and failure.

The aim of the present work is to develop Bio-active glass coating which is to be used for orthopedic dental implants to improve the quality of life for people who have lost their teeth. At present, in India as well, Central Glass and Ceramic Research Institute (C.G.C.R.I), Kolkata, is involved in development of titanium base dental implants which is to be coated by Bio-active glass With and without Hydroxy Apatite (HA).

2. EXPERIMENTAL PROCEDURES

The composition of the coating materials was determined in such a way so that it’s calculated thermal expansion coefficient (Using Winkelmann and Schott factors) can match with the metal substrate[3].

The glass was prepared using a conventional glass melting procedure. The appropriate amounts of reagents/raw materials quartz (SiO_{2}), CaCO_{3},[2] dry soda ash (Na_{2}CO_{3}), decahydrated borax (Na_{2}B_{4}O_{7},10H_{2}O), TiO_{2}, di-ammonium hydrogen phosphate[(NH_{4})_{2}HPO_{4}], were mixed together properly in water. The batch composition of the glass was shown in table-IV.3. The mixture was first dried at 100°C for 1 hr then melted in air at temperature 1600°C for 3 hrs. in a Pt crucible. The experimental variables used during glass melting were shown in table-IV.4. The melt was quenched in to water and obtained flaky glass particles, dried and stored for subsequent use. The frit was subsequently milled along with different mill additives in aqueous medium in a porcelain jar for 72 hrs with HA (20%) and without HA. The oxide composition [4] and batch composition of prepared glass given in table: 1 and table: 2.

Table: 1. Oxide composition of the prepared glass (mol %)

|        | SiO_{2} | Na_{2}O | CaO | P_{2}O_{5} | B_{2}O_{3} | TiO_{2} |
|--------|--------|--------|-----|-----------|-----------|--------|
|        | 59 - 61| 8 - 12 | 21 - 25| 2 - 5 | 2 – 5 | 0.5 – 2.5 |

Table: 2. Batch composition of the prepared glass (wt %)

|        | SiO_{2} | Na_{2}B_{4}O_{7}, 10H_{2}O | Na_{2}CO_{3} | CaCO_{3} | (NH_{4})_{2}HPO_{4} | TiO_{2} |
|--------|--------|---------------------------|--------------|---------|---------------------|--------|
|        | 42 - 44| 5 - 7                      | 10 - 13      | 28 - 331| 7 – 10              | 0.5 – 2.5 |
Titanium [5] metal and SS316L was coated by the HA free glass and glass with 20% HA [6]. The coated sample is depicted in Fig: 1, Fig: 2, Fig: 3 and Fig: 4.

3. Results and discussion
3.1: DTA/TGA ANALYSIS
The Fig: 5 show a typical DTA/TGA pattern of the bioactive glass composition [7] investigated. The TGA graph indicates that the glass is thermally stable and no significant wt. loss is observed during heating to 800°C.

The DTA pattern showed one endothermic peak at 41.0°C probably due to moisture removal, one exothermic peak at 416.6°C, which may be due to structural changes, and one endothermic nucleation temperature at 631.8°C and exothermic growth temperature at 756.5°C.

Fig: 5. DTA/TGA Analysis of bioactive glass (without HA) coated sample
3.2: SURFACE ROUGHNESS:
The surface roughness (Ra in micron) of coated sample (with & without HA) is depicted in table-3. Qualitatively we analyzed that, the coating with low Ra value having better adherence to the metal surface. It may be due to proper fusion and settling of molten glass coating material to the metal surface.

Table: 3. Surface Roughness value of coated sample

| Name of the Sample         | Average Ra Value (in micron) | Standard Deviation (in micron) |
|----------------------------|------------------------------|--------------------------------|
| SS-316L without HA        | 2.406                        | 0.397                          |
| SS-316L with 20% HA       | 1.569                        | 0.284                          |
| Ti without HA             | 1.797                        | 0.338                          |
| Ti with 20% HA            | 1.806                        | 0.370                          |

3.3: SURFACE REFLECTANCE:
Surface reflectance of coated samples were measured using Double Beam Ratio Recording Spectrophotometer Model no.UV3101PC. Results of surface reflectance measurements of the coated samples indicate that the average surface reflectance is in the range of 0.1-0.7% in the range of 500-1500 nm wavelength of radiation. The results are in agreement with the surface roughness measurement data.

3.4 RESULTS OF IN-VITRO ANALYSIS OF COATED SAMPLE IN SBF SOLUTION
The change in weight of the coated samples with time of duration of immersion in SBF [8] solution is shown in table 4

Table: 4. Change in weight of coated Ti and SS-316L samples in Simulated Body Fluid

| Sample name | Initial | After 1 week | After 2 weeks | After 3 weeks | After 4 weeks |
|-------------|---------|--------------|---------------|---------------|---------------|
| TB          | 2.2079  | 2.2079       | 2.1978        | 2.1970        | 2.1967        |
| TH          | 2.2271  | 2.2271       | 2.2271        | 2.2270        | 2.2170        |
| TU          | 2.1754  | 2.1755       | 2.1756        | 2.1757        | 2.1859        |
| SB          | 2.5462  | 2.5462       | 2.5459        | 2.5456        | 2.5353        |
| SH          | 2.2392  | 2.2392       | 2.2389        | 2.2385        | 2.2382        |
| SU          | 2.3384  | 2.3385       | 2.3385        | 2.3485        | 2.3487        |

TB & SB: Titanium & Stainless steel coated with Developed Bioactive glass
TH & SH: Titanium & Stainless steel coated with Developed Bioactive glass containing 20% HA
TU & SU: Uncoated Titanium & Stainless steel

The weight change data (Fig: 6) indicates that the reaction of the coating with the S.B.F fluid was initially very negligible but with progressive duration of exposure the reaction rate increases resulting in increasing weight loss. The initial inertness of the coating may be attributed to the presence of a silica network on the as fired coating surface. Once the reaction was initiated the reaction rate
becomes almost constant throughout the rest of the period as was reflected in the change in weight values. The results also indicate that incorporation of HA lower down the reaction rate of the resultant coating. The metal controls used are naturally very less reactive.

![Graph showing weight loss over time](image)

**Fig: 6 Change in Weight loss**

### 3.5 COATING ADHERENCE:
The adherence of Developed Bioactive glass (with or without HA) coating on Ti and SS-316L metal surface [9] was tested by 3-Point Bending Moment using INSTRON 5500R [10]. The result is shown in table: 5. the results indicate that the coatings are strongly adhered to the metal substrates.

**Table: 5. Results of thee point bending moment of coated samples**

| Name of the samples              | Load to break the coating (N) | Stress to break the coating(MPa) |
|----------------------------------|------------------------------|----------------------------------|
| Bioactive Glass Coated Ti        | 460 – 580                    | 700 – 860                        |
| Bioactive Glass Coated SS-316L   | 460 – 580                    | 680 – 720                        |
| HA containing Bioactive Glass Coated Ti | 430 – 540               | 575 – 750                        |
| HA containing Bioactive Glass Coated SS-316L | 420 – 530           | 525 – 630                        |

### 4. CONCLUSIONS
The work is still under progress but till its output showing the attractive results to reach our target for developing better strengthening bioactive glass coating. The in vitro behavior of the silicate glass coatings analyzed in this work is similar to that of bulk glasses. Coatings with silica content lower than 60wt% precipitated apatite during in vitro testing. The mechanism of apatite formation is similar to that described by Hench for Bioglass®. However, due to their lower silica content, the thermal expansion of these coatings is higher than that of Ti and the tensile thermal stresses generated during processing drove the slow growth of cracks in S.B.F. The cracks eventually reached the interface and initiated delamination. Higher silica coatings did not form apatite but were more resistant to corrosion and slow crack growth. At the moment, graded coatings that have glasses with high silica content in contact with the metal and a low silica glass on their surface are under
development in order to improve their long term stability while maintaining a good biological response.

HA particles were incorporated into these coatings to promote increased bioactivity. The effectiveness of Bio-glass incorporation depended on the softening temperature of the glass coating, with higher softening temperatures leading to increased degradation of the Bio-glass. This was not the case for HA. Incorporation of ~20% of either particle type was successfully accomplished without cracking or loss of adhesion to the melted substrate.

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