

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 1, January 2017

Development and Analysis of Glass & Ceramic Based Coating Material for Orthopaedic Implants to Increase Better Bonding and Stability

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ABSTRACT: Over a period of time a number of biomaterials have been developed and are used for hard tissue and joint replacement those are Stainless steel (SS-316L), Co-Cr alloy, Titanium (Ti) and its alloy, ceramics and Polymer especially Ultra High Molecular Weight Polyethylene (UHMWPE) and Alumina (Al_2O_3). These biomaterials for its suitable mechanical properties, nontoxic behavior, and bio-compatibility can be used as orthopedic implant materials. Titanium, Ti-6Al-4V (alloy) and SS-316L are widely used as materials for orthopedic implants, due to their advantageous mechanical properties and nontoxic behavior but one of the major drawback 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. 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. Bone cement (Poly methyl methacrylate) is used to improve the implant fixation but it may result in deterioration of the adjacent bone and failure. 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. What has been needed is a coating that adheres to the metal surface of the implant and also promotes the formation of Hydroxy apatite (the inorganic component of bone) and better bonding with better stability. The glass ceramic coating material developed according to Appen, the best agreement between the calculated coefficient of expansion to match the thermal expansion coefficient with the metallic implants and studied is suitable for coating Ti and SS-316L substrates by conventional vitreous enameling technique. The glass ceramic coating upon controlled heat treatment produces a glass ceramic containing wollastonite as crystalline phase. The adherence of coating on Ti and SS-316L metal surface was tested by 3-Point Bending Moment using INSTRON 5500R. The results indicate that the coatings are strongly adhered to the metal substrates. The Surface roughness, surface reflectance and DTA/ TGA analysis of coating showed a very good result as per the requirement. Further the successful implants need a porous coating that can be fabricated by using different pore formers like naphthalene powder or other organic materials. This new coating technique overcomes the disadvantages of the systematic treatment and might potential solution for such treatment in the long run.

KEYWORDS: Coating, Stainless steel (SS-316L), Co-Cr alloy, Titanium (Ti), Ultra High Molecular Weight Polyethylene (UHMWPE), Alumina (Al_2O_3), Hydroxy apatite [$Ca_{10}(PO_4)_6(OH)_2$], Instron, bending moment, DTA/ TGA, Thermal expansion coefficient.

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I. INTRODUCTION

A biologically active coating that enables metal implants to bond with bone could significantly extend the lifetime of artificial hips, knees, and other medical reconstructive devices. More than \$2 billion is spent yearly in this country on hip and knee implants, plates and pins for broken bones, dental implants, and other reconstructions. An estimated 11 million persons in the United States have at least one such medical implant and this number is growing as the population receiving implants increases. 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 have been implanted, creating wear and tear that shortens implant lifetimes. For example, according to the National Center for Health Statistics, hip implants generally fail after 15 years and one out of every five hip-replacement surgeries is performed to replace one of these failed implants. What is needed is a coating that adheres to the metal surface of the implant and also promotes the formation of Hydroxy apatite (the inorganic component of bone), reported Antoni Tomsia, a materials scientist with Berkeley Lab's Materials Sciences Division which has maintained a long-term program for the study of ceramic/metal interfaces. Working with physicist Eduardo Saiz, Tomsia has developed a silicate glass that is bioactive, and a simple "enameling procedure" whereby metal implants can be coated with micron-sized (20-200 microns thick) layers of this glass. These glass layers can be fine-tuned at the metal-glass and glass-bone interfaces so that the coating binds with both metal and bone.

It is impossible to design a single coating that will serve all purposes, so what they have done is to create a set of two to three graded layers of coating, reported Tomsia. The glass is cheap to make and the enameling is inexpensive.

In the enameling process used by Tomsia and Saiz, precursor powders are painted on the metal surface and the implant is then annealed at temperatures of 800°C to 900°C. Titanium and cobalt-chromium remain solid at these temperatures but the glass becomes liquid. The liquid glass will uniformly coat the surface of even the most intricately shaped implant, a marked advantage over plasma coatings that must be sprayed onto a surface.

There have been previous tests of ceramic coatings on metal implant surfaces but the rates at which the ceramics and metals expanded under the heat of processing differed so much that large stresses were introduced. These thermal stresses led to cracks in the ceramics at the metal interface, which weakened the adhesion between the two surfaces. Furthermore, chemical reactions between the ceramic and the metal, particularly titanium, weakened the implant.

They have adjusted the coatings so that the thermal coefficient of the glass matches that of the metal alloy. This eliminates the introduction of thermal stresses during processing.

II. AIM AND SCOPE OF THE PRESENT WORK

The aim of the present work is to coat the metal implants with ceramic based material employing a simple vitreous enameling technique. The metals used in this work were Ti and SS-316L because they are especially appropriate for implants under high stress, such as hip and dental implants. We have synthesized the coating material to match thermal expansion coefficient of the metal, and can be used to enamel the Ti and SS-316L.

The scope of the present work is limited to develop the formulation of the bio-glass, the appropriate methodology to coat the metal samples and study the following parameters DTA/TGA analysis, particle size analysis, and study the surface roughness, adherence. The present work includes development of coating material [1] which can be used for coating metal implant surfaces. These coated metal implant surfaces attributes several advantageous properties like enhanced better bonding through tissue in growth in the porous coating surface on the implant. These properties can be tailored to control load distribution in the implant bone interface resulting in longer implant life and better efficiency.

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III. PRESENT STATUS OF THE WORK

The Glass coatings on Ti were prepared using a simple enameling technique. Compositions of the glasses (on the SiO₂-Na₂O-K₂O-CaO-MgO-P₂O₅ system) [2, 3, 4] was tailored to match the thermal expansion of Ti. By controlling the firing atmosphere, time, and. Temperature, it was possible to control the reactivity between the glass and the Titanium metal and to fabricate coatings (25–150 μm thick) with excellent adhesion to the substrate. The glasses are based on Hench's Bioglass[®] (glasses in the SiO₂-Na₂O-CaO-P₂O₅ system) (5, 6, 7, 8) and have silica contents ranging from 44 to 70 wt%. Coatings on Ti was successfully fabricated using glasses whose silica content was >55%. At lower silica contents, the coatings cracked due to the high stresses that result from the large difference in thermal expansion between the glasses and the metals. The optimum firing temperatures ranged between 800 to 840°C at times up to 1 min in air or 15 min in N₂. The results for glass coating indicated that coatings containing better bonding and stability with implant.

IV. MATERIALS AND METHODS

A. PREPARATION OF COATING MATERIALS AND COATED SAMPLE.

The composition of glass (shown in Table-IV.1) was tailored to obtained thermal expansion coefficient close to that of Ti (84.95×10⁻⁷/°C) and SS-316L (138.95×10⁻⁷/°C). The detailed properties of the substrate metal used in this study were shown in table-IV.2. The glass was prepared using a conventional glass melting procedure. The appropriate amounts of reagents/raw materials quartz (SiO₂), CaCO₃, dry soda ash (Na₂CO₃), decahydrated borax (Na₂B₄O₇·10H₂O), TiO₂, diammonium hydrogen phosphate[(NH₄)₂HPO₄], 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 1400°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 48 hours. The processing parameters were shown in table-IV.5. In order to prepare the coatings, a suspension of the glass powder in water was deposited on Ti (1" length, 5.05mm dia) and SS316L (1" length, 3.99mm dia) and Ti plates (1"×1"×3 mm) those had been previously sandblasted and cleaned in acetone or ethanol. Afterwards the coatings were dried in air at 90°C - 100°C for 45 minutes and fired at temperature 800°C to 820°C. The details of coating parameters were shown in table-IV.6.

The photographs of coated Ti and SS316L samples were shown in Fig: 1 and Fig: 2 respectively. The DTA/TGA of glass coating material was analyzed by simultaneous thermal analysis using NETZSCH GERATEBAU GmbH Model no.409C.

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

SiO ₂	Na ₂ O	CaO	P ₂ O ₅	B ₂ O ₃	TiO ₂
58 - 60	9 - 11	22 - 24	2 - 4	2 - 4	1 - 2

Table: IV.2. The properties of the metals studied

Name of the sample	Specific Gravity	Ultimate TensileStrength (MPa)	Young's Modulus (GPa)	α (10 ⁻⁷ /°C)	Hardness (Knoop)
Ti	4.5	333.63	143.62	84.95	1800-2600
SS-316L	7.8-8.2	1006.37	236.99	138.95	1200-9600

α= Thermal expansion co-efficient from RT to 600°C.

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Table: IV.3. Batch composition of the 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
43 - 44	6 - 7	11 - 12	29 - 30	8 - 9	1 - 2

Table: IV.4. Experimental variables for preparation of glassy coating material

Glass melting temperature	1400°C
Batch charging temperature	1200°C
Melting atmosphere	Oxidizing
Fritting condition	Quenched in water

Table: IV.5. Processing parameters of the coating material

Mill additions	Frit (85 – 100 %), Clay (0 – 5%),
Milling time	48 hrs in small porcelain jar
Specific gravity of slip	1.23
Fineness	- 325mesh BS sieve

Table: IV.6. Coating parameters

Coat thickness	50 – 60 (μ)
Firing temperature	800 – 820°C
Firing time	5 – 10 mins

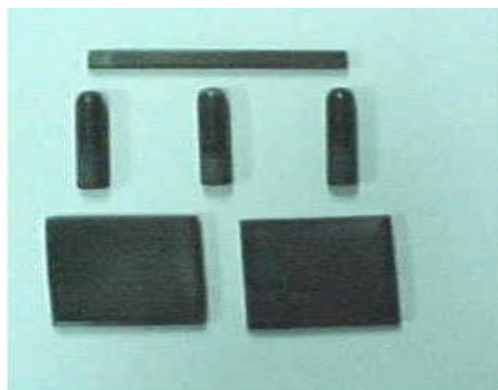


Fig. 1. Glass coated Ti samples

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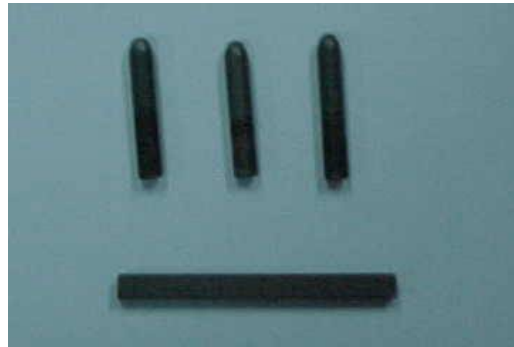


Fig: 2. Glass coated SS-316L samples

B. METHOD TO CALCULATE THERMAL EXPANSION COEFFICIENT OF GLASS.

To calculate the coefficient of expansion of glasses, about 18 series of factors are known. In practice, to calculate the expansion coefficient we normally use the Winkelmann and Schott factors [9], supplemented by other workers for opacifiers and colorants. The discrepancy between the values calculated from these factors and those measured for glasses is on average $\pm 10\%$.

According to Appen, the best agreement between the calculated coefficient of expansion and those found experimentally is noted if the glass composition is expressed in molecular percentage and the calculated factors obtained for the wider range of temperature are used. The coefficient is calculated from the formula

$$\alpha \times 10^7 = \frac{\sum a_i \times \alpha_i}{100}$$

where a_i is the content of oxides in the glass in mol % and α_i is the averaged numerical characteristic of the partial coefficient of expansion of oxides (Table-IV.7).

Values for α are either taken directly from table-IV.7 (for oxides with constant mean characteristics for α_i) or pre-calculated from the approximate and empirical formula (for SiO_2 , TiO_2 , B_2O_3 , PbO)

The values of α_{SiO_2} are calculated from the formula:

$$\alpha_{\text{SiO}_2} \times 10^7 = 38 - 1(a_{\text{SiO}_2} - 67)$$

Where a_{SiO_2} is the amount of silica in the glass in mol %.

If the amount of silica is less than 67% then the value of $\alpha_{\text{SiO}_2} \times 10^7$ is tentatively assumed to be 38.

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Table: IV.7. Factors for calculating coefficients of thermal expansion of glasses

Components	Mean volume coefficient of expansion ($3\alpha \times 10^7$)		Mean linear coefficient of expansion ($\alpha_i \times 10^7$)
	Winkelmann and Schott	Mayer et al	Appen
	20 – 150		20 – 400
SiO ₂	0.8	—	5 – 38
TiO ₂	1.3	4.1	(+30) – (– 15)
ZrO ₂	—	2.1	– 60
SnO ₂	—	2.0	– 45
Al ₂ O ₃	5.0	—	– 30
B ₂ O ₃	0.1	—	(0) – (–50)
Sb ₂ O ₃	—	—	75
As ₂ O ₃	2.0	—	—
BeO	—	4.7	45
MgO	0.1	—	60
CaO	5.0	—	130
SrO	—	—	160
BaO	3.0	—	200
ZnO	1.8	—	50
CdO	—	—	115
PbO	3.0	4.2	130 – 190
MnO	—	2.2	105
1/2Mn ₂ O ₃	—	—	105
FeO	—	—	55
1/2F ₂ O ₃	—	4.0	55
CoO	—	4.4	50
NiO	—	4.0	50
CuO	—	2.2	30
Li ₂ O	—	—	270
Na ₂ O	10.0	—	395
K ₂ O	8.5	—	465
CaF ₂	—	2.5	180
Na ₂ SiF ₆	—	—	340
Na ₃ AlF ₆	—	7.4	480
NaF	—	7.4	—
AlF ₃	—	4.4	—
Cr ₂ O ₃	—	5.1	—
Sb ₂ O ₅	—	2.5	—
P ₂ O ₃	2.0	—	140
CeO ₂	—	4.2	—

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To determine the calculated factor for boric anhydride we use the equation:

$$\alpha_{B_2O_3} \times 10^7 = 12.5 (4 - \phi) - 50$$

where, ϕ is the ratio of the total number of moles of oxide Me_2O , CaO , BaO , to the number of moles of B_2O_3 .

If it is greater than 4, then $\alpha_{B_2O_3} \times 10^7$ is tentatively assumed to be a constant and equal to 50.

When calculating ϕ the presence in the glass of oxides MgO , ZnO , PbO is not taken in to account. In the case of the simultaneous presence in the glass of boric anhydride and alumina, the coefficient of ϕ is determined from the formula:

$$\phi = (a_{Me_2O} + a_{MeO} - a_{Al_2O_3}) \div a_{B_2O_3}$$

where a_{Me_2O} and a_{MeO} are the total contents of monovalent and divalent oxides in mol %. The values α_{TiO_2} and α_{PbO} are calculated from the formula:

$$\alpha_{TiO_2} \times 10^7 = 30 - 1.5(a_{SiO_2} - 50);$$

$$\alpha_{PbO} \times 10^7 = 130 + 5(a_{Me_2O} - 3);$$

V. RESULTS AND DISCUSSION

V.1: DTA/TGA ANALYSIS

The Fig: 3 show a typical DTA/TGA pattern of the coating material composition investigated. The TGA graph indicates that the glass is thermally stable and no significant wt. loss is observed during heating to $800^\circ C$.

The DTA pattern showed one endothermic peak at $41.0^\circ C$ probably due to moisture removal, one exothermic peak at $416.6^\circ C$, which may be due to structural changes, and one endothermic nucleation temperature at $631.8^\circ C$ and exothermic growth temperature at $756.5^\circ C$. These later peaks correspond to nucleation and growth of wollastonite (Ca-silicate) phase later identified by XRD.

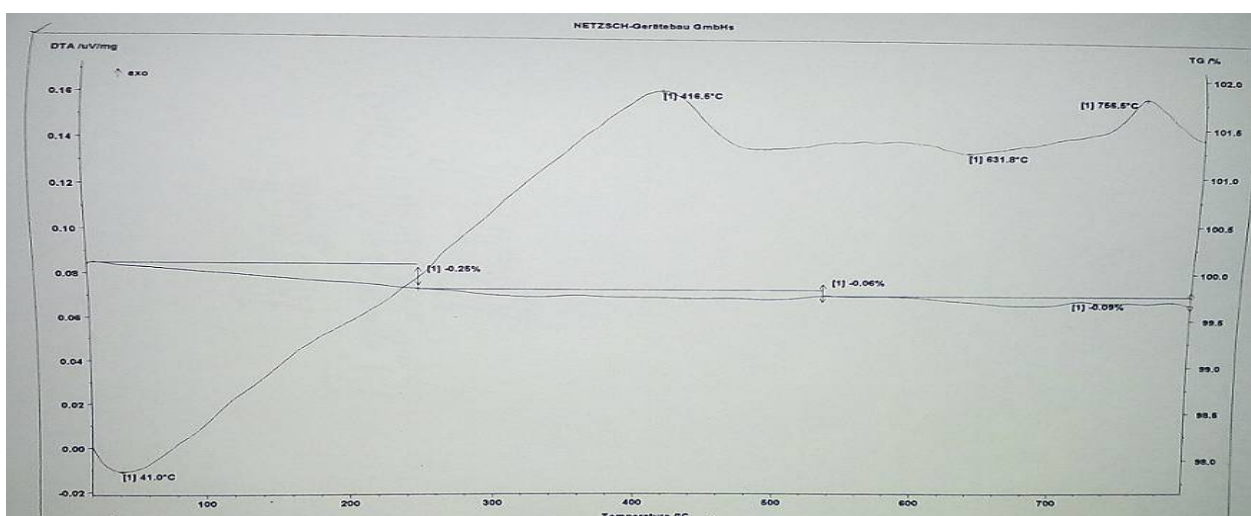


Fig.3. DTA/TGA Analysis of coated sample

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V.2: PARTICLE SIZE ANALYSIS

The particle size of the glass coating material (slip) was analyzed by MASTERSIZER2000Ver.3.01. The result was shown in Fig: 4 which showed the particle size of glass coating material used in this experiment was within the range of 0.142(μm) to 14.159(μm).

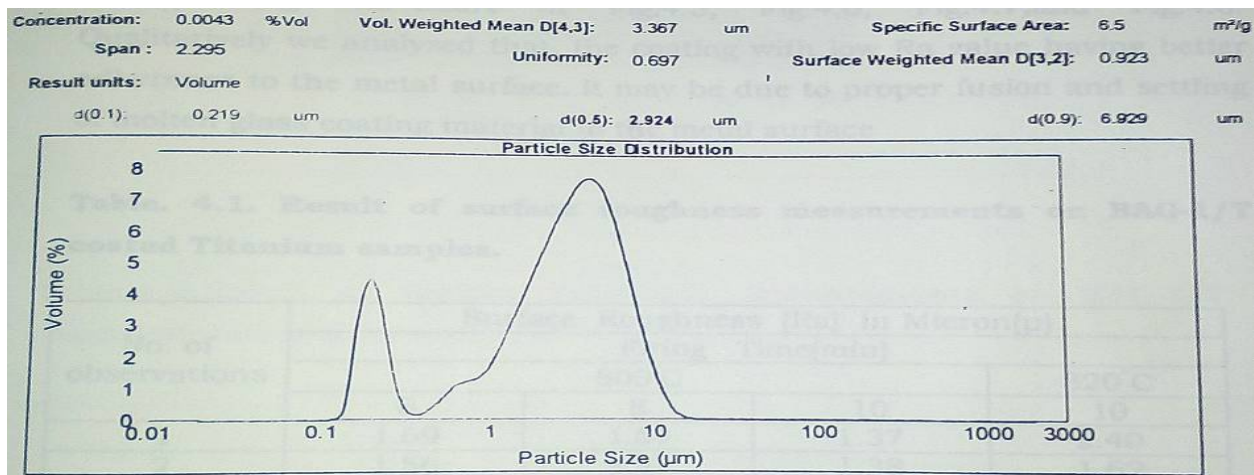


Fig:4. Particle size analysis of glass coating materials

V.3: COATING CHARACTERIZATION

SURFACE FINISH:

The surface roughness (Ra in micron) of coated Ti and SS-316L (fired at different temperature with different soaking time) samples were measured using Surtronic-3P. The results were shown in table-IV.8 and table-IV.9 respectively with their corresponding Bar-Chart in Fig:5 and Fig:6 respectively. 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:IV.8. Result of surface roughness measurements on glass coated Titanium samples.

No. of observations	Surface Roughness (Ra) in Micron(μ)			
	Firing Time(min)			
	800 $^{\circ}$ C		820 $^{\circ}$ C	
	6	8	10	10
1	1.69	1.69	1.37	2.40
2	1.56	2.37	1.38	1.62
3	2.21	1.92	1.74	1.56
4	1.19	1.47	1.87	1.50
5	1.87	1.63	1.73	1.60
6	1.63	1.26	1.95	2.12
7	1.12	2.19	1.90	2.53
8	1.38	2.13	1.92	1.52
9	1.87	1.63	1.59	1.95
10	1.91	1.68	1.68	1.60
Avg	1.643	1.797	1.713	1.840
ST _{DEV}	0.342	0.338	0.212	0.386

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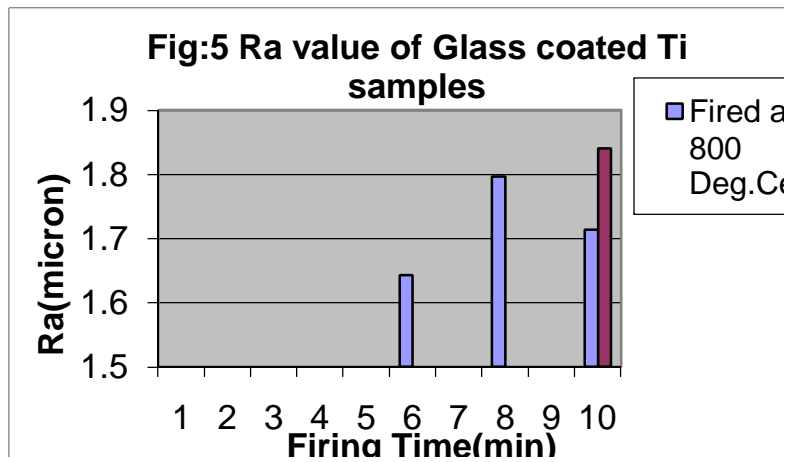


Table:IV.9. Result of surface roughness measurements on glass coated Stainless steel samples.

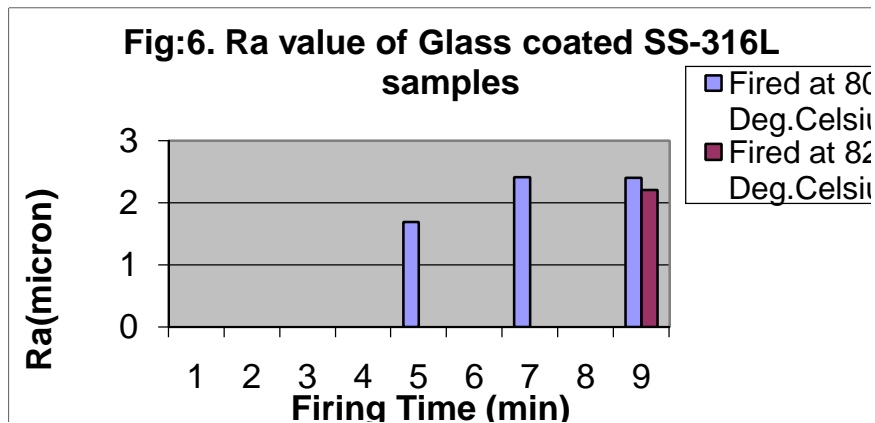
No. of observations	Surface Roughness (Ra) in Micron(μ)			
	Firing Time(min)			
	800 $^{\circ}$ C			820 $^{\circ}$ C
	5	7	9	9
1	1.38	1.97	2.45	1.79
2	1.56	2.18	2.51	2.16
3	2.22	1.99	1.88	1.74
4	2.11	2.59	2.92	2.07
5	1.65	2.81	2.55	2.29
6	1.64	2.36	2.27	2.20
7	1.38	2.94	2.39	2.06
8	1.31	2.19	2.50	2.94
9	2.04	2.04	2.44	2.22
10	1.66	2.99	2.11	2.61
Avg	1.690	2.406	2.402	2.208
ST _{DEV}	0.323	0.397	0.277	0.356

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COATING ADHERENCE:

The adherence of glass coating on Ti and SS-316L metal surface was tested by 3-Point Bending Moment using INSTRON 5500R. The result is shown in table-IV 10. The results indicate that the coatings are strongly adhered to the metal substrates.

Table.IV.10. Results of Adherence measurements

Name of the samples	Load to break the coating (N)	Stress to break the coating(MPa)
Glass coated Ti	450 – 550	680 – 840
Glass coated SS-316L	450 – 550	660 – 700

VI: CONCLUSION & FUTURE PROGRAM

The glass ceramic coating material developed and studied is suitable for coating Ti and SS-316L substrates by conventional vitreous enameling technique. The glass ceramic coating upon controlled heat treatment produces a glass ceramic containing wollastonite as crystalline phase.

The scope of future work is enormous. The present work is not complete and need detailed investigation on coating property like XRD analysis, SEM analysis after the in vitro test of the coated samples to evaluate its bio-activity.

Further the successful implants need a porous coating that can be fabricated by using different pore formers like naphthalene powder or other organic materials.

ACKNOWLEDGEMENT

I would like to express my deep sense of gratitude to my respected teachers and research guides Dr.S.Datta (scientist, Central Glass & Ceramic Research Institute, Kolkata) for their constant guidance and supervision encouraged me to carry out this work.I also extend my thanks to Dr.M.K.Sinha & Dr.A.Dasgupta (scientists, Central Glass & Ceramic Research Institute,Kolkata) for their help and support. Last but not least I must acknowledge the encouragement, cooperation and help of fellow students, technical and non-technical staffs of Central Glass & Ceramic Research Institute and School of Bio-Science & Engineering during the period of research.

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