Experimentation Detail

4.1 SELECTION OF MATERIAL

4.1.1 Metal Preparation

The candidate material namely, austenitic stainless steel SS 304, LCS1018 and Copper were selected for experimental investigations. The chemical compositions of these materials are given in Table 4.1. Four specimen of each metal (SS304, copper and LCS) were cut to dimension 40 mm × 40 mm × 5 mm. The metal specimens were initially cleaned with soap solution and then cleaned with acetone to remove all dust and grease from the metal specimen.

Table 4.1: Chemical compositions of metal specimens

Material	Chemical Composition Wt%												
	C	Mn	P	S	Cr	Cu	Ni	N	Si	Bi	Sb	Pb	Fe
SS304	0.08	2	0.045	0.030	18		12	0.10					Balance
LCS1018	0.16	0.90	0.040	0.040					0.40				Balance
Copper			0.005	0.005		99				0.01	0.002	0.005	0.005

4.1.2 Surface Roughness Measurement

The metal specimen was then polished with different grit size (cloth polished, 120, 220, 320) emery paper on "Bainpol Metco" polishing machine to achieve a different level of surface roughness. A total 48 specimen (16 SS304, 16 Copper and 16 LCS1018) and each specimen of SS304, copper and LCS were polished with grit size paper cloth, 120, 220 and 320 at least with three repetitions. The specimens were then again cleaned with soap solution and acetone after polishing with emery paper. The surface roughness of metal specimens R_a values was then measured with the help of "Bruker Dektek XT 100"profilometer.

4.1.3 Oxide Layer Mass Gain and Oxide Layer Thickness

The specimens were then pre-oxidized at 700 ° C for 3 minutes by heating the metal specimen in the muffle furnace with a heating rate as shown in Figure 4.1.

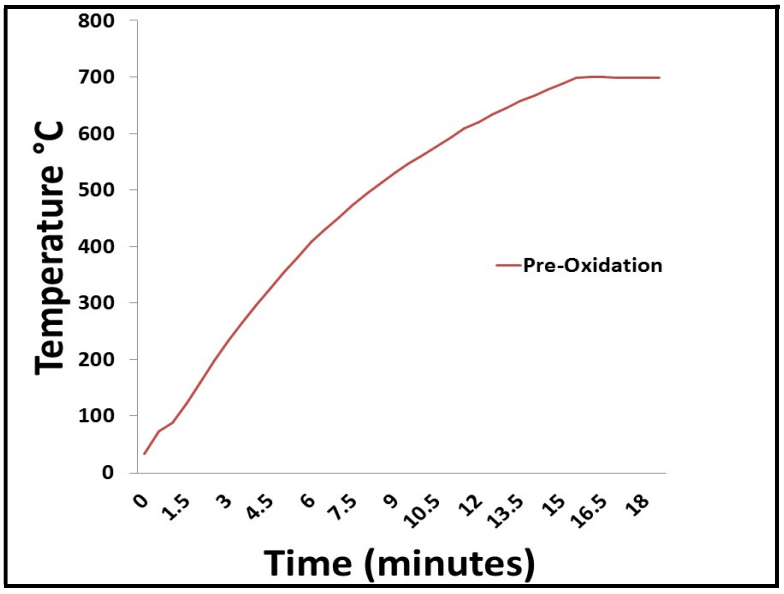


Figure 4.1: Heating curve of Specimen for pre-oxidation study

The specimens were then cooled in furnace till room temperature was achieved and weighed again after pre-oxidation. The change in weight of metal specimen after peroxidation divided by its surface area leads to oxide mass gain (g/cm^2). In order to measure the oxide layer thickness the specimens were cut parallel to the thickness of the metal specimen and then mounted in die filled over with resin. The dimension of metal specimen for the measurement of oxide layer thickness (μm) was taken 10 mm ×10 mm× 5 mm and mounted specimen was then polished with emery paper in order to get a uniform flat surface. The oxide layer thickness was measured with the help of "Dewinter" optical microscope.

4.1.4 Types of Oxide Phase In Metal Specimens

The nature of oxide phase formed during the fabrication of glass-metal assembly was evaluated using X-ray diffraction measurement using "Bruker Axis Automated Powder X-Ray Diffractometer"at a scan speed of 0.02°/minutes. The XRD measurement for all metal specimens was taken at three conditions namely, fresh condition (as-received), pre-oxidation condition and joining condition of the metal specimen.

4.1.5 Wettability of Borosilicate Glass Sealant

4.1.5.1 Glass Pallet Pre-formation

The borosilicate glass tubes were initially broken into small pieces and then washed with acetone to clean all grease particles from the glass. The original glass was available in the dense form and to obtain the required size, pre-formation of glass was required. After breaking and cleaning with acetone, all the broken pieces were put into 10% HF solution, whose function is to remove dirt from the glass. The broken pieces were dried using drier and then crushed in a mortar-pestle. Crushed glass was then passed through 50-micron mesh size sieve so as to obtain the required size. The final shape achieved for glass pallet was a cylindrical shape having dimensions 10 mm diameter and 5 mm thickness.

4.1.5.2 Contact Angle Measurement

In order to study the wetting behavior of borosilicate glass over these specimens, high-temperature wettability study was carried out over these metal specimens. The glass pallet was then placed over the center of these metal specimens and complete assembly was heated in a muffle furnace at 980 °C for 20 minutes. The melting of glass over SS304 metal was carried out at a heating rate of 20 °C/minute. The diameter and height of melted glass was measured and the contact angle was measured using following mathematical relation:

$\theta/2 = \tan^{-1}(h/d)$ ……(1)

d=diameter of drop

h=height of drop

θ=contact angle

In this analysis, the glass pallet was assumed to be part of a sphere. The geometry of pallet was analyzed by measuring the diameter and height of apex. The values of angle obtained through mathematical relation described the wettability of glass pallet over the metal specimen.

4.2 SELECTION OF GLASS-METAL JOINT DESIGN

4.2.1 Compression Joint Geometry Selection Procedure

The austenitic stainless steel SS304 was considered to be the suitable candidates for joining glass with metal after the pre-oxidation, wettability and microstructure examination. Therefore, to join SS304 metal with borosilicate glass tube for the development of glass-metal joint, the selection of joint geometry was an important factor. Initially, the glass tube inner surface was placed over the outer surface of SS304 metal ring as shown in Figure 4.2(a). The complete assembly was then heated locally to 980 °C with the help of an induction heating set-up.

During heating, it was observed that the metal expansion was faster than glass, and resulted in breakage of glass as shown in Figure 4.2 (b). In other trials, the glass tube was placed in a tight fit over the inner surface of metal tubes Figure 4.2 (c). The complete assembly was then heated from room temperature to 980 °C in an induction heating set-up. It was observed that metal expands faster than glass in the outward direction and a gap was formed between the metal ring and glass tube as presented in Figure 4.2 (d).

To overcome the problem originating from the design condition shown in Figure 4.2 (c) and Figure 4.2 (d), the borosilicate glass sealant powder was used to fill the gap between the metal ring and glass tube as shown in Figure 4.2 (e). During heating of assembly from room temperature to joining temperature, the metal expands faster than the glass. The glass sealant started expanding in outward direction along with metal. However, when the complete assembly was cooled to room temperature, metal contracts to the original position and compressive stresses were developed in glass as shown in Figure 4.2(f).

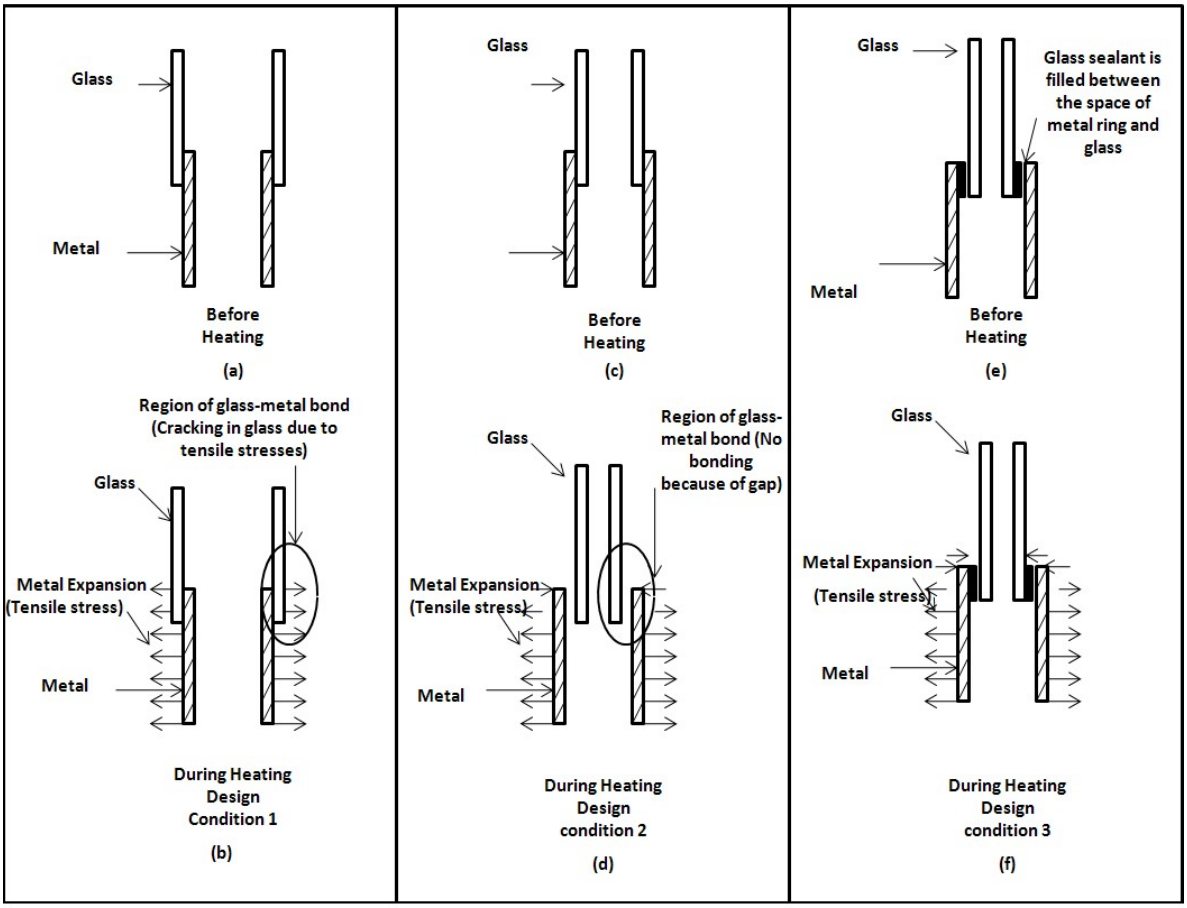


Figure 4.2: Different design condition of glass–metal joint

As a result of this experimentation, the compressive joint was formed between glass tube and metal ring with the help of the glass sealant. From the above experimentation, compression glass-metal joint geometry was obtained to be a suitable geometry for glass-metal joint fabrication.

4.2.2 Selection of Induction Coil Design

The induction setup (horizontal hardening) was used to perform experimentation. Initially, induction coil was attached in horizontal direction with induction heating plant as shown in Figure 4.3 (a), and the direction of induction heat was in radially inward direction. The orientation of coil was modified to vertical direction as per requirement of compression glass metal joint fabrication as shown in Figure 4.3(b, d). Another coil was designed in the form of flat spiral coil in order to concentrate induction heat on the surface of the SS304 metal specimen as shown in Figure 4.3(c) for in-situ wettability study (explained in section 4.11).

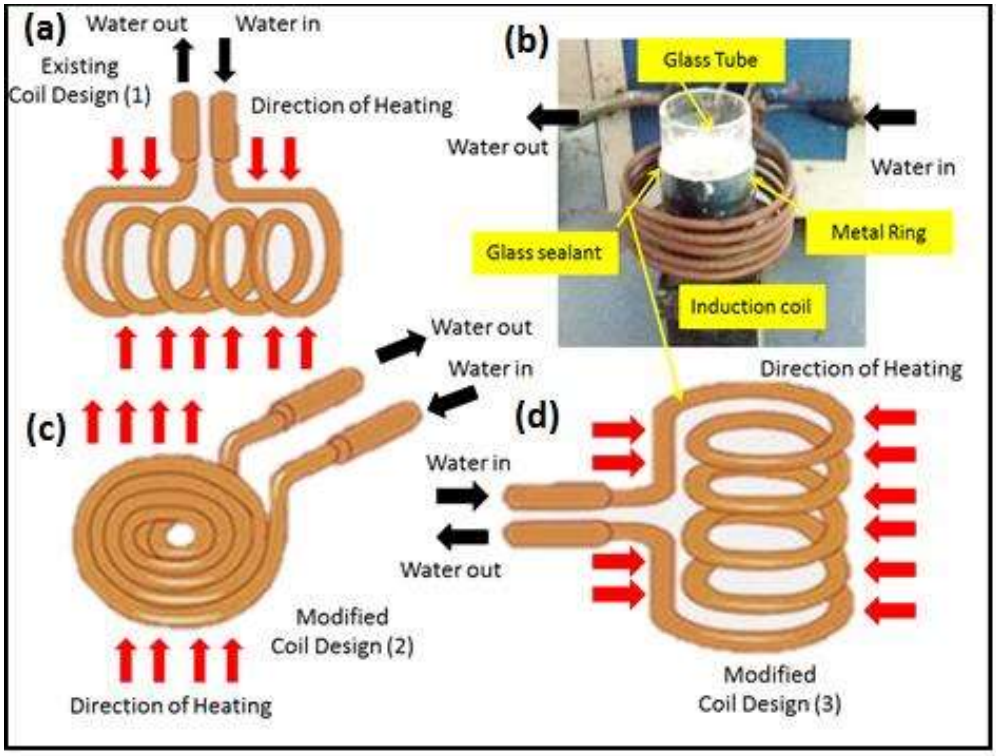


Figure 4.3: Induction coil design modification for experimentation

The glass-metal joint was fabricated in induction furnace according to the following process parameter of induction furnace as shown in Table 4.2.

Table 4.2: Induction heating setup process parameter

S.no	Heat Input(kW)	Time(minutes)	Temperature(°C)
1	350	0-2	30-650
2	460	2-3	650-760
3	525	3-4	760-840
4	630	4-5	840-930
5	730	5-6	930-1010
6	630	6-7	1010-930
7	525	7-8	930-840
8	460	8-9	840-760
9	350	9-10	760-650
10	Machine shut down	10-13	Till room temperature

4.3 DESIGN OF GLASS-METAL JOINT

The compression type of joint design was considered to be the suitable design from pre-experimentation result [explained in section (4.2.1)]. The designing of suitable glass sealant for the development of compression glass-metal joint between borosilicate glass tube and SS304 metal ring is very important issue.

4.3.1 Compression Glass-Metal Joint Geometry Fabrication

In order to design a mechanical robust glass-metal joint, it has been recognized that generated stresses after fabrication must be kept as low as possible. The higher value of metal thickness leads to cracking of glass tube in glass-metal seal as shown in Figure 4.4.



Figure 4.4: Cracking of glass tube because of higher metal ring thickness

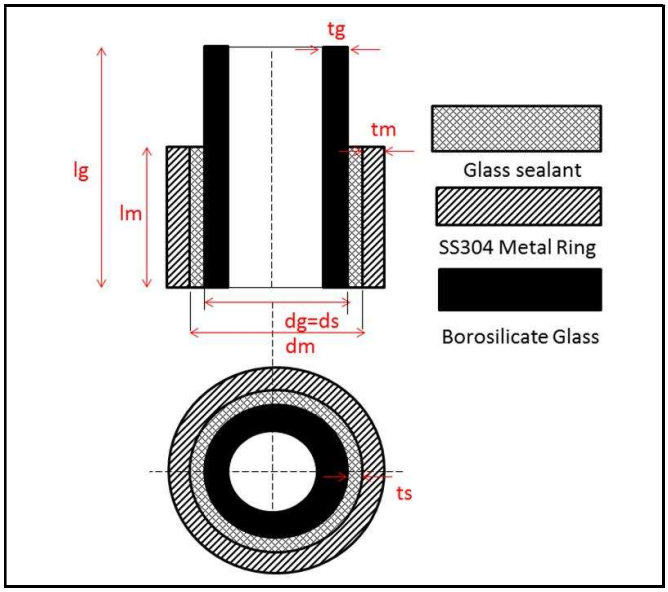


Figure 4.5: Geometry of compression glass-metal joint

The glass-metal joint using compression geometry as shown in Figure 4.4,

Table 4.3: Dimension of different glass-metal joint specimen used

Specimen	Glass Tube Dimension(mm)			Metal ring Dimension(mm)			Glass Sealant(mm)	
	Outer Diameter of glass tube (dg)	Thickness of glass tube (tg)	Length of glass tube(lg)	Inner Diameter of metal ring (dm)	Metal Ring Thickness (tm).	Length of Metal Ring (lm).	Inner Diameter of glass sealant (ds).	Thickness (ts)
1	26	2	50	29	2.5	25	26	1.5
2	26	2	50	29	2	25	26	1.5
3	26	2	50	29	1.8	25	26	1.5
4	26	2	50	29	1.6	25	26	1.5
5	26	2	50	29	1.4	25	26	1.5
6	26	2	50	29	1.2	25	26	1.5
7	26	2	50	29	1	25	26	1.5
8	26	2	50	29	0.8	25	26	1.5
9	26	2	50	29	0.6	25	26	1.5
10	26	2	50	29	0.4	25	26	1.5

The joint was fabricated using 2.5 mm metal thickness and found that cracking of glass tube occurred at the interface of glass-metal joint as shown in Figure 4.4. The magnitude of stresses generated at glass-metal joint assembly was related to the metal thickness of glass-metal joint. The geometry of compression glass-metal joint is as shown in Figure 4.5. In order to overcome the cracking issue in glass-metal joint interface due to higher intensity of residual stress, different metal thickness joint ring were prepared with dimension shown in Table 4.3.

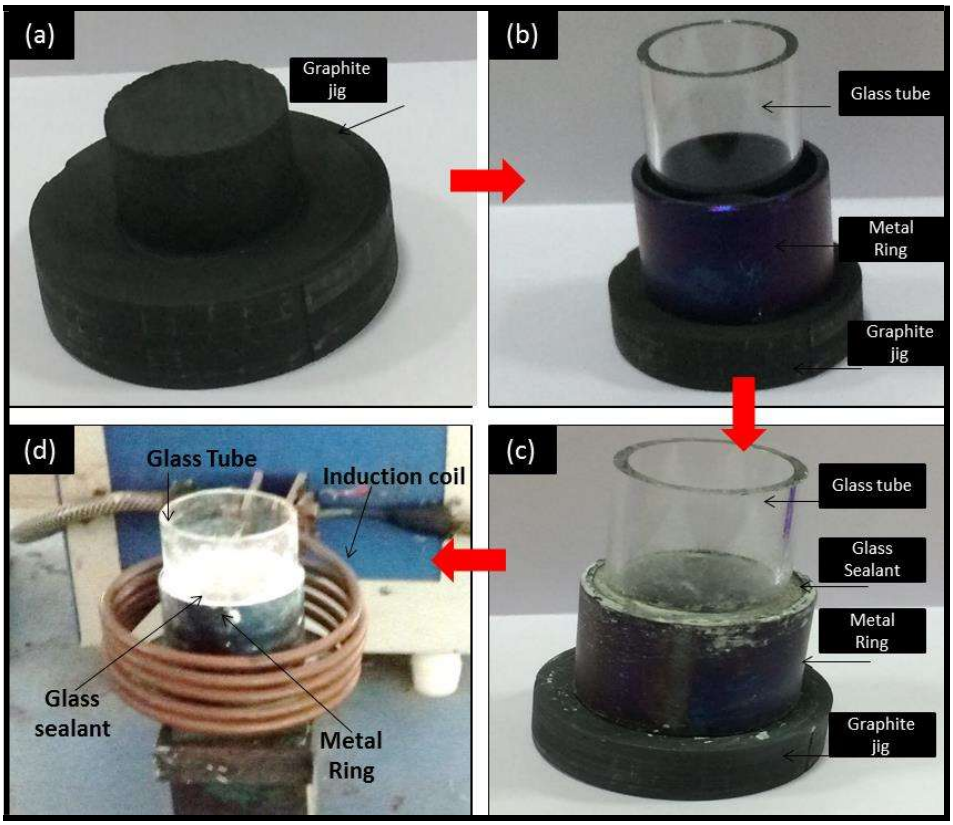


Figure 4.6: Experimental procedure of glass-metal joint fabrication

Initially, metal ring of austenitic stainless steel SS304 was available in the dimension of 28 mm internal diameter with 2.5 mm thickness. In order to achieve metal ring of different sizes as shown in Table 4.3, the required dimension of each specimen was prepared on lathe machine using turning and internal boring operation. Different sizes of SS304 metal ring and borosilicate glass tubes having the chemical composition (SiO_2 81%, B_2O_3 13%, Na_2O 4%, Al_2O_3 3%) were first washed with soap solution and then with acetone to remove dust and grease from metal rings and glass tubes respectively.

Prior to fabrication, metal rings were pre-oxidized in the muffle furnace at 700 °C for 3 min. The pre-oxidation process parameters were selected on the basis of wettability and spreading behavior of borosilicate glass over SS304.The borosilicate glass tube was then placed over graphite jig which was prepared by step turning operation on lathe shown in Figure 4.6(a). The glass tube inner surface was then placed over graphite jig shown in Figure 4.6 (b). The gap between the glass tube and pre-oxidized SS304 metal ring was then filled with glass sealant (SiO_2 40 %, B_2O_3 54%, Na_2O 4%, Al_2O_3 2%) as shown in Figure 4.6(c).The complete glass-metal joint assembly was then heated with the help of induction heating setup from room temperature to 980 °C as shown in Figure 4.6(d).

4.3.2.1 Residual Stress Measurement after Glass-Metal Joint Fabrication

The fabricated glass-metal joint assembly of different metal thickness as shown in Table 4.3, was then examined for residual stresses, on the glass tube using "PS-100-BS" polarimeter as shown in Figure 4.7(a).

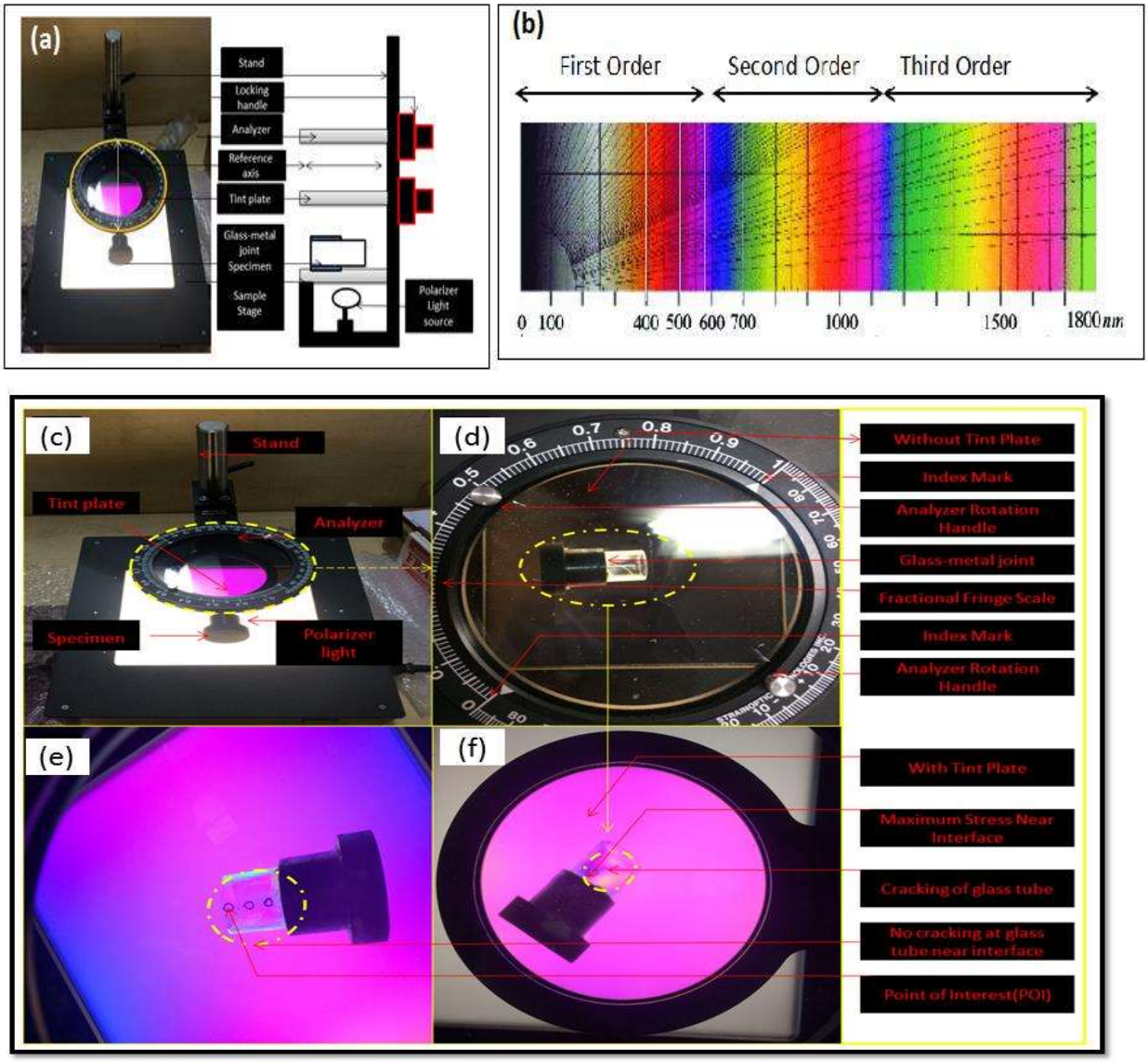


Figure 4.7: (a) Experimental Set-up of stress measurement in the glass metal joint, (b) Color fringe scale to calculate (n) , (c) Scaled up view of polarimeter, (d) Rotational scale to show index marl 0-1 and (f) scale,(e, f) showing the intensity of point of interest and maximum stress intensity at the interface).

The polarimeter worked on the principle of photoleasity and uses photoelastic color to measure stress distribution in the glass material using analyser rotation [Aden et.al, 2008]. During the experiment, glass-metal joint assembly after fabrication was cleaned with acetone and then placed on sample stage between light source and analyzer shown in Figure 4.7 (c). The axis of glass-metal joint assembly was kept parallel to the reference axis and analyzer position was set to index marks 0-1 position. The 0-1 position is marked with index mark as shown in Figure 4.7(d).

The Point of interest (POI), where the intensity of stress is to be measured was marked with round circle with the help of a marker in the glass tube as shown in Figure 4.7(e). The intensity of stress in the glass tube was shown in white and gray color as shown in Figure 4.7(d). In order to see the intensity of stress in the form of color fringes, tint plate was installed in between the polarizer and analyzer as shown in Figure 4.7(f). The analyzer was rotated in clockwise direction to obtain maximum colour intensity at the point of interest as shown in the Figure 4.7(e) . The fractional fringe scale value corresponding to maximum colour intensity was noted to obtain the (f) value. The value of n (lower full order fringe number) was calculated from the intensity of colour shown in Figure 4.7(b).

The obtained value of 'f' was further used to calculate fringe order using equation (2) as below.

$N = n + f$ …… (2)

The fringe order (N) obtained from equation [2] was further used to calculate stress in the glass tube near glass-metal joint interface as shown below. Where 'n' is the lower full order fringe number (0,1,2,3,4)

Stress (MPa) = $\frac{\delta nm}{t_{mm} * C_{Brewester}}$ ……..(3)

Retardation (δnm) was calculated by multiplying "N" with wavelength of light λ (for glass 565 nm according to ASTM F218 standard). The term t_{mm} and $C_{Brewester}$ are the thickness of glass tube and the Brewster constant (being different for different type of glass). In present experimentation $C_{Brewester}$ = 3.3 was taken which is a standard for borosilicate glass [Stain Disk Manual].

4.3.2.2 Thermal Expansion Mismatch in Glass-Metal Joint

In the glass-metal joint, thermal expansion mismatch between glass and metal tube was calculated after the examination of residual stress experimentally using standard [International standard Practice]. The effect of metal thickness on thermal expansion mismatch was examined with the help of 'Polarimeter'.

Stress values obtained using polarimeter was further used for calculating thermal expansion mismatch as per equation (4)

$$\left(\frac{\Delta l}{l}\right)_t = \frac{S(1-\mu_g)}{E_g F} \quad \text{……..(4)}$$

$\left(\frac{\Delta l}{l}\right)_t$ =Total thermal expansion mismatch from room temperature to sealing temperature

μ_g =poison ratio of glass

F=shape factor

$$F=\frac{(kr^4+3r^2+4r)}{(kr^4+4r^3+6r^2+4r+1/k)}$$

$$k=\frac{Em}{Eg}$$

$$r=\frac{tm}{tg}$$

E_m , E_g , t_m, and t_g are Young's modulus and thickness of metal and glass respectively.

The glass sealant obtained though sealant design experimentation was used to fabricate compression glass-metal joint which was used further to study the pre-oxidation behaviour, wettability, adhesion strength and interfacial study.

4.4 DESIGN OF SUITABLE GLASS SEALANTS

Initially, the glass sealant was available in the form of borosilicate glass tube having chemical composition (81% SiO_2, 13%B_2O_3, 2%Al_2O_3, and 4%Na_2O) and glass tube was crushed in the form of powder.

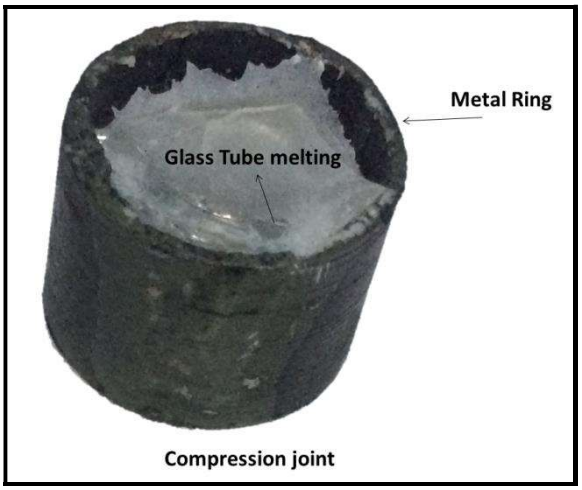


Figure 4.8: Melting of glass tube along with glass sealant using compression joint geometry

The glass sealant was filled between the space of metal ring and glass tube. During the fabrication of compression glass-metal joint, borosilicate glass tube as well as glass sealant were melted simultaneously and no compression glass-metal joint was achieved. The condition of glass-metal joint using borosilicate glass sealant is as shown in Figure 4.8.

4.4.1 Role of SiO_2 / B_2O_3 Ratio on the Glass Sealant Properties

The melting glass sealant before the melting of borosilicate glass tube was the reason due to which no joint was achieved. In order to solve the issue, borosilicate glass sealant composition was tailored by tailoring the $nSiO_2/nB_2O_3$ ratio with constant composition of Na_2O and Al_2O_3. The glass sealant composition was prepared by mixing different ingredients of glass purchased from Sigma Aldrich (Na_2O, SiO_2) and Fisher Scientific (B_2O_3 and Al_2O_3). All the components were weighed according to design matrix with different specimen code shown in Table 4.4 and mixed properly with the help of mortar pestle.

Table 4.4: Glass sealant design matrix

Glass Sealant code	Composition (Wt %)				SiO_2/B_2O_3 Ratio
	SiO_2	B_2O_3	Al_2O_3	Na_2O	
BG1	81	13	2	4	6.23
BG2	75	19	2	4	3.94
BG3	70	24	2	4	2.91
BG4	60	34	2	4	1.76
BG5	50	44	2	4	1.13
BG6	40	54	2	4	0.74

4.4.1.1 Effect of SiO_2 / B_2O_3 Ratio on wettability

In order to examine the wetting behavior of different glass sealant over the SS304metal substrate, glass sealant pallet was formed by adding 3% polyvinyl alcohol (PVA) in glass sealant powder of approximately 2.0 g of powder in 10 mm diameter die made up of steel in the hydraulic press. A minimum pressure of 100 kg/cm^2 was applied over the die for 1 minute to form pallets, while above 100 kg/cm^2 the pallet often fractured and hence it was ejected from the die during pressing. The glass sealant pallet was then removed from the die and baked in the oven till 120 °C in order to remove PVA from glass pallet. The detail procedure of glass sealant formation is given in (Figure 1 appendix). Later, the glass sealant was then placed over the pre-oxidized austenitic stainless steel SS304 metal specimen as shown in Figure 4.9, and placed in the muffle furnace. The pre-oxidation of the SS304 metal specimen was carried out at the pre-oxidation temperature of 700°C for 3 minutes.

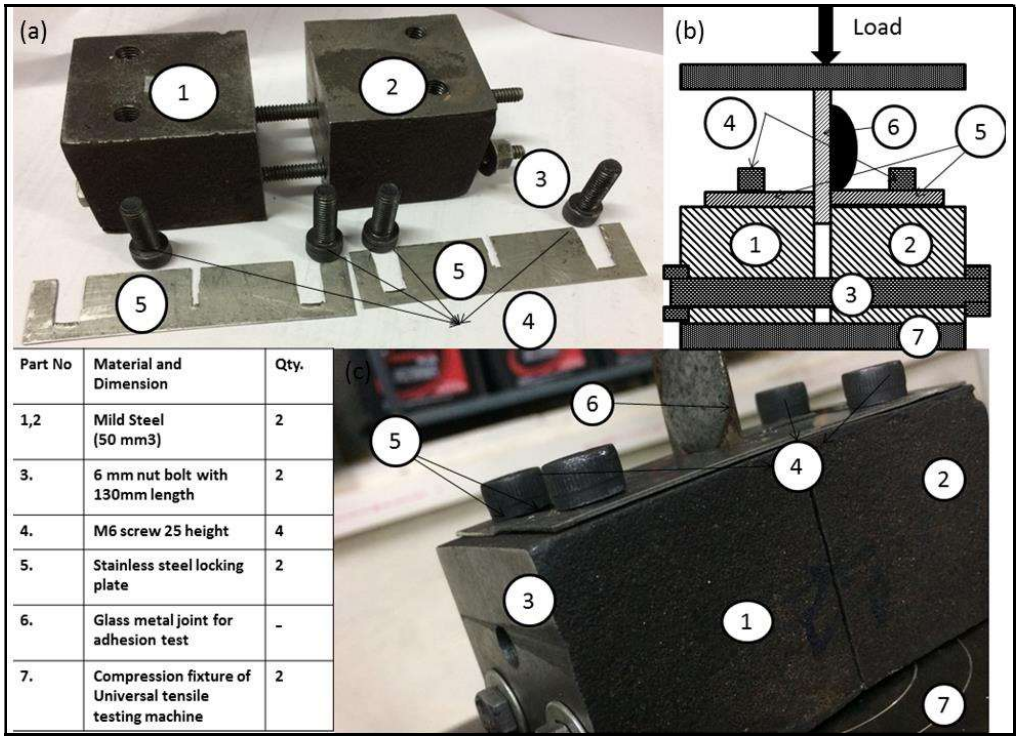


Figure 4.9: Glass pallet specimens over pre-oxidized austenitic stainless steel 304 metal specimen

The entire glass sealant specimen was heated in batch using muffle furnace to the 980 °C temperature. The spreading area (mm^2) contact angle (θ) was then measured with the help of image capturing system.

4.4.1.2 Effect of SiO_2 / B_2O_3 Ratio on Adhesion strength

Adhesion strength testing between glass sealant with SS304 metal substrate was performed under compression loading condition. The glass sealant pallet was melted over pre-oxidized metal specimen and adhesion between glass sealant pallet and SS304 metal specimen were measured using specially-designed fixture as shown in Figure 4.10 (a) where load presses only on the metal part (dimension: 25 mm x 25 mm x 1.5 mm) which was fixed by locking the stainless steel plate as shown in Figure 4.10 (a-c). Compression testing was performed by placing specially designed fixture in UTM "Universal Tensile Testing Machine of Lloyd Instruments, Ez-50 model". The load where glass detaches from the surface of the metal substrate was recorded in a computer attached with the UTM. The dimensions and material used for fabricating this fixture is shown in Figure 4.10.



Part No	Material and Dimension	Qty.
1,2	Mild Steel (50 mm3)	2
3.	6 mm nut bolt with 130mm length	2
4.	M6 screw 25 height	4
5.	Stainless steel locking plate	2
6.	Glass metal joint for adhesion test	-
7.	Compression fixture of Universal tensile testing machine	2

Figure 4.10: Specimen mounting holder for adhesion test

4.4.1.3 Effect of SiO_2/ B_2O_3 Ratio on Thermal and Structural Properties

4.4.1.3.1 X-Ray Diffraction Measurement

X-Ray diffraction (XRD) analyses of different glass sealant was performed using a diffractometer (Bruker Axis Automated Powder X-Ray Diffractometer) to confirm the amorphous nature of different glass sealant with Cu Kα(λ=1.54A°) radiation. During the experimentation, the scan speed was kept 0.02°/ minutes.

4.4.1.3.2 Fourier Transform Infrared Spectroscopy (FTIR) Measurement

The infrared absorption spectra of different glass sealant powder were recorded using Fourier Transform Infrared (FT-IR) Spectrometer (Infrared Fourier Vacuum Spectrometer Vertex 70v -1101). The KBr powder was used as a reference material for FTIR measurement and the spectra of the specimen was measured in the wavenumber ranging from 400-4000 cm^{-1} with a resolution of 2 cm^{-1}. The transmittance results of glass sealant were plotted against wave number in cm^{-1}.

4.4.1.3.3 Thermal Studies Measurement

Thermal studies of different glass sealant powder were carried out using DTA instrument (Exstar TG/DTA, 6300). The heat input of glass sealant specimen was plotted against temperature from 30 °C to 1200 °C in the alumina crucible. The heating rates of glass sealant powder sample were taken 20 °C/min using N_2 as the inert atmosphere. The nitrogen gas flow rate was kept 200 ml/minutes during DTA analysis. The results were then plotted against % weight loss of glass sealant with temperature. The thermal stability of glass sealant was measured with TGA analysis.

4.4.1.3.1.4 Thermal Conductivity Measurement

The thermal conductivity of different glass sealant powder was carried out using a principle of Fourier law of heat conduction. The experimental set-up of thermal conductivity is shown in Figure 4.11. The glass sealant pallet, having dimensions 25 mm× 25 mm× 1.5 mm were made with the help of hydraulic press using pallet making die. The glass sealant pallet making procedure was same as glass pallet (Section ***4.4.1.1*** *page 31*). The pallet was then placed on the heating plate shown in Figure 4.11 and thermocouples T1 and T2 were installed to measure the temperature of glass sealant raised due to heating of plate.

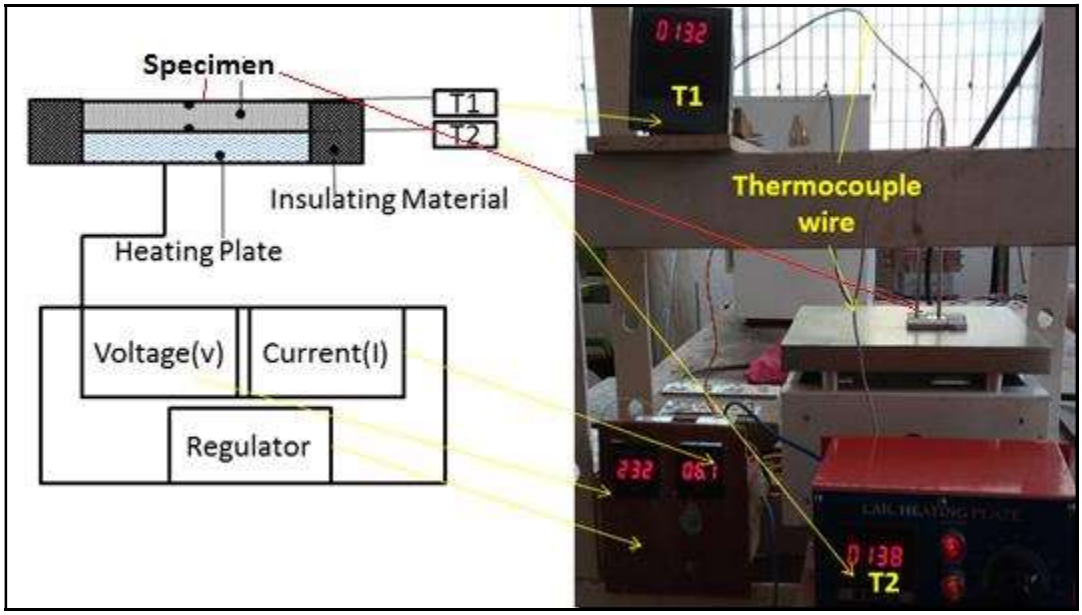


Figure 4.11: Thermal conductivity experimental set-up

Heat input=Q=-KA$\frac{dT}{dx}$

K=conductivity of glass sealant

Q=Heat input to heating plate

A=Area of glass sealant

dT= Difference of temperature °C at above and lower face of plate

dx =Thickness of glass sealant

Q=V×I

V=voltage corresponding to heating plate

I=Current flowing through heating plate

The heat input to the heating plate was measured by calculating the efficiency of the heating plate. The austenitic stainless steel SS304 metal specimen was taken as reference material having known thermal conductivity value.

4.4.1.4 Effect of SiO_2 / B_2O_3 Ratio on Morphology and Elemental Composition of Glass sealant

To see the morphology of glass sealant after melting, 10 g of each glass sealant powder of the homogeneous mass was kept in the graphite crucible and heated in the muffle furnace. The solidified glass sealant was then removed from the graphite crucible and polished to achieve the smooth surface finish as shown in Figure 4.12.



Figure 4.12: Glass sealant pallet after melting in furnace

Specimen size of dimensions 1 mm × 1 mm × 3 mm was cut from the specimen and examined under scanning electron microscope. The Energy dispersive x-ray spectroscopy analysis of specimen was taken to get the elemental composition of glass sealant pallet.

4.4.2 Design of Experiment

The best glass sealant composition was obtained corresponding to BG6 Specimen where lower value of glass transition temperature Tg and lower value of crystallization temperature was found. The adhesion strength and wettability of glass sealant was also observed to be a maximum for $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ chemical composition. In order to see other suitable glass sealant, lot of experimentation needs to be carried out. To overcome the experimentation problem, design of experiment approach was utilized to find other suitable glass sealant.

During the design of experimentation, the composition of glass sealant were designed using extreme vertices design method which has been studied by [Jindal.S et al., 2013; Bhandari.D et al., 2016] for welding application. According to this method, constraint mixture components containing their upper and lower limit were selected mathematically as

$0 \leq \alpha i \leq xi \leq \beta i \leq 100$

And

$\sum_{i=1}^{K} x_i = 100$

Where i=1, 2, 3, 4…….k are the number of component of glass sealant mixture and αi, βi are the upper and lower limit of glass sealant component.

The chemical composition of glass sealants was selected on the basis of SiO_2-B_2O_3-Na_2O ternary phase diagram system shown in Figure 4.13

The upper and lower range of component composition is marked with in the red area. The other components, TiO_2, CaO, MgO and BaO having 2.5% of each component is mixed in glass sealant mixture. In order to add these components in glass sealant consisting SiO_2, Al_2O_3, B_2O_3 and Na_2O the sum of glass sealant composition is scaled down to the total of 90%.

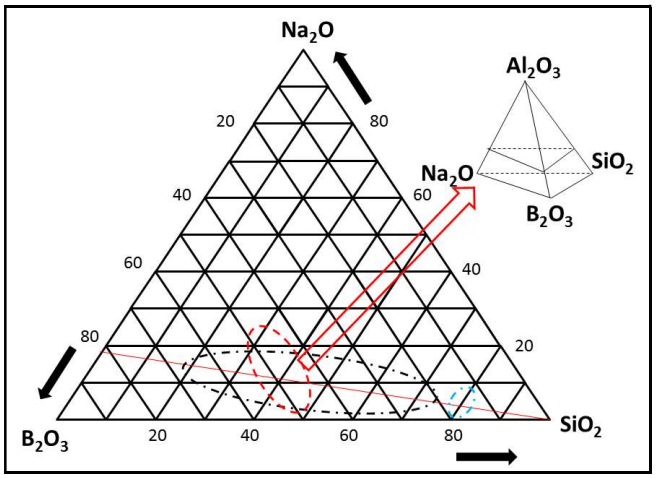


Figure 4.13: Experimental phase diagram of SiO_2-B_2O_3-Na_2O glass system

The upper and lower limit of glass sealant used in present study was selected based on experimentation and on the basis of adhesion strength and wettability. During the experimentation study, the percentage of SiO_2 was reduced by increasing B_2O_3 and found that wettability and adhesion strength of glass-sealant with metal increases.

The $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ composition (BG6) was found to be an optimum composition where maximum adhesion and wettability was obtained and this composition was selected on the basis of experimentation carried. Therefore, the composition of SiO_2, Al_2O_3, B_2O_3 and Na_2O glass sealant ingredient was tailored near to $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ composition are given in equations [1-4]. In order improve the strength of glass sealant with metal specimen, TiO2, CaO, MgO, and BaO component were added in the fixed percentage of 2.5% with a sum of 10%.

$30 \leq SiO_2(x_1) \leq 43$ ……..(1)

$45 \leq B_2O_3(x_2) \leq 55$ …… (2)

$1 \leq Al_2O_3(x_3) \leq 5$ ……..(3)

$1 \leq Na_2O(x_1) \leq 5$ ……..(4)

$\sum_{i=1}^{4} x_i = 90$ ……..(5)

Eighteen set of glass sealant compositions were designed by varying the composition of four elements SiO_2, B_2O_3, Al_2O_3 and Na_2O having upper and lower limit mentioned in equation [1-4] using extreme vertices mixture design methodology as shown in Table 4.5.

The polyhedral space of each experiment according to glass sealant mixture design is as shown in Figure 4.14. The output of glass sealant response characteristics for K component is given in the form of second order regression model as given in equation (6).

$Y = \sum_{i=1}^{k} b_i x_i + \sum_{i<j} \sum^{k} b_{ij} x_i x_j$ ……..(6)

Where bi and bij are least square model regression coefficients .The individual and combined effect of mixture components in regression model is represented by $b_i x_i$ and $b_{ij} x_i x_j$ respectively.

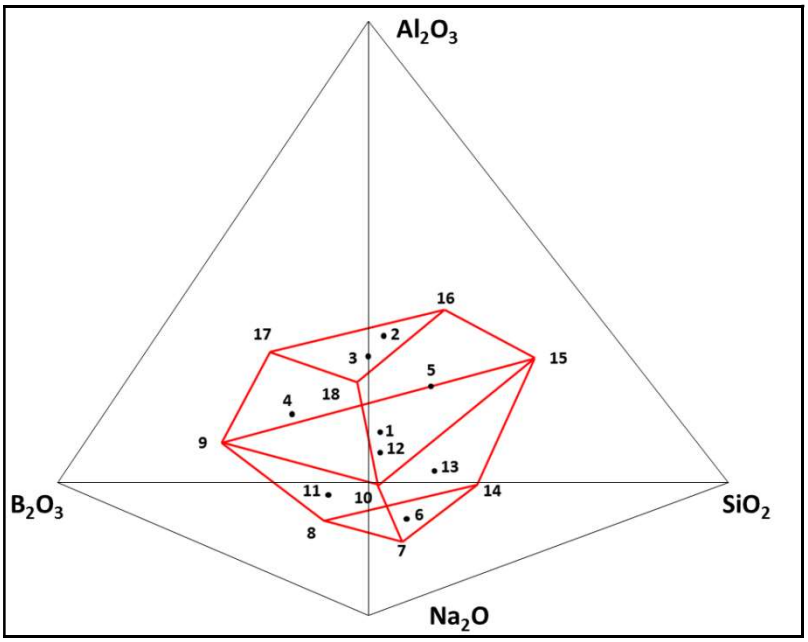


Figure 4.14: Polyhedral design on the basis of mixture design methodology

The wettability, adhesion strength, thermal and structural measurement over this eighteen glass sealant specimens was also carried out. The experimentation procedures are same as discussed in section (4.3.2.1.(1-4)]. The suitable glass sealant was selected on the basis of SiO_2/B_2O_3 ratio and DOE methodology study which was further used to fabricate the compression glass metal joint.

Table 4.5: Design matrix of glass sealant formulation

Experiment Number	Ingredients of glass sealant			
	SiO_2	Al_2O_3	B_2O_3	Na_2O
1	39	1	45	5
2	33.9	2.9	50.3	3
3	30	1	55	4
4	33.5	3	48.5	5
5	30	4	55	1
6	31	2	55	2
7	35	1	50.8	3
8	43	1	45	1
9	33	1	55	1
10	30	3.2	53.6	3
11	39	5	45	1
12	35	3.2	50.8	1
13	30	5	50	5
14	33.5	5	48.5	3
15	39	3	45	3
16	30	1	54	5
17	30	5	54	1
18	35	5	45	5

4.5 SELECTION OF PRE-OXIDATION TIME AND PRE-OXIDATION TEMPERATURE

The pre-oxidation condition (700 for 3 minutes) was obtained to be a suitable condition on the basis of experimentation carried out in section (4.1). In order to see the effect of pre-oxidation time on the oxide layer thickness, oxide layer mass gain and types of oxide formed. To study the oxide layer formation on SS304 alloy specimen, 16 (SS304) metal specimens of dimensions 25 mm × 25 mm × 1.5 mm were repeatedly heated in a muffle furnace at 700 °C for 2, 3, 4 and 5 minutes. The initial weights of these metal specimens before heating were measured and recorded using electronic precision weighing balance. After cooling to room temperature, the specimens were again weighed using a precision weighing balance with an accuracy of ±0.1mg. The oxide layer thickness formed on metal specimen corresponding to different pre-oxidation conditions was measured using an optical microscope "Dewinter". The pre-oxidized metal specimens were cut along the thickness of metal specimen to dimension of 10 mm ×10 mm square area and 1.5 mm thickness and were then mounted in resin filled specimen holder as shown in Figure 4.15.

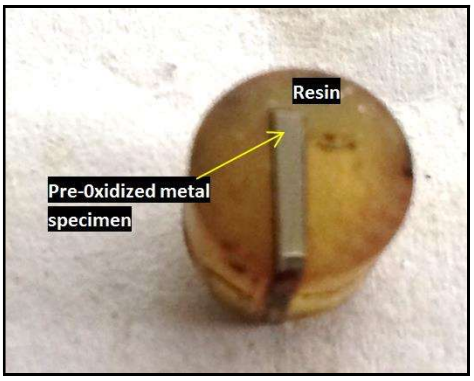


Figure 4.15: Pre-oxidized metal specimen mounted on resin

4.6 TYPES OF OXIDE FORMED AFTER PRE-OXIDATION IN SS304 METAL SPECIMEN

In order to analyze the type of oxides formed after pre-oxidation at 700 °C for 2, 3, 4 and 5 minutes, metal specimens were analyzed for X-ray diffraction using "Bruker Axis Automated Powder X-Ray Diffractrometer" with Cu Kα(λ=1.54A°) radiation. During the experimentation, the scan speed was 0.02°/min. The morphology of oxide present at the metal surface was analysed using scanning electron microscopy "Zeiss make Scanning Electron Microscope". The types of oxide phase obtained with XRD were validated with the help of Fe to O ratio obtained through "Energy Dispersive X ray Spectroscopy".

4.7 WETTABILITY STUDY OF $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ GLASS SEALANT OVER SS 304 METAL SPECIMEN AT DIFFERENT PRE-OXIDATION TIME

In order to examine the wetting behavior of different glass sealant over the pre-oxidized SS304 metal substrate at 700 °C for 2, 3, 4 and 5 minutes, $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ glass sealant pallet was formed. The round glass sealant pallet forming procedure was same as explained in (*Section 4.4.1.1 page 31*).The wettability study of $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ glass sealant pallet was carried out over the SS304 metal specimen. The SS304 metal specimen was pre-oxidised at 700 °C for 2, 3, 4 and 5 minutes. The glass pallet was then placed over the pre-oxidised metal specimen and complete glass sealant and metal specimen assembly heated in muffle furnace at 980 °C for 20 minutes. The assembly was then allowed to cool in the furnace itself. The contact angle and spreading area of glass sealant over metal specimen was measured using image capturing system. A reference object having known dimensions was marked in

front screen in order to calculate and correlate image pixel size measured with respect to reference object.
The actual height of glass sealant pallet was 10 mm and the number of pixel obtained in still image captured were 230 pixel
1 mm of length =230/10 pixel
Similarly, 1 pixel represents 10/230 mm
This measurement was used to calculate the height (h) and diameter (d) at different stages during melting and solidification to obtain the value of contact angle using formula
$\theta/2 = \tan^{-1}(h/d)$ ……(1)
Where, d= diameter of the glass sealant pallet
h=height of glass sealant pallet
θ=contact angle measured

4.8 ADHESION STRENGTH OF $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ GLASS SEALANT WITH SS304 METAL SPECIMEN

The adhesion strength of $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ glass sealant pallet with pre-oxidized metal specimen pre-oxidized at different pre-oxidation time (2, 3, 4 and 5 minutes) was carried out at 700°C. The experimental procedure of adhesion strength measurement is same as discussed the (section 4.3.21.).

4.9 INTERFACIAL STUDY OF $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ GLASS SEALANT OVER SS304 METAL SPECIMEN

In order to study the diffusion of molten glass sealant over austenitic stainless steel SS304 metal specimen, the glass sealant pallet was melted over metal substrate pre-oxidized at 700 °C for 3 minutes (most suitable pre-oxidation condition where maximum wettability and adhesion was obtained) and having cross-sectional area of 25 mm ×25 mm with 1.5 mm thickness. The morphology and presence of oxide at glass-metal interface of the above mentioned specimen a 10 mm× 10 mm ×1.5 mm square specimen was cut from the above mentioned specimen. The specimen was then mounted in a sample holder filled with resin as shown in (Figure 4.15). The sample was then polished using specimen cloth polishing machine to obtained flat surface. The polished specimen was then analysed using "Bruker Axis Automated Powder X Ray Diffractometer". The X-ray diffraction pattern obtained was then analyzed with the help of software (ICDD) "International Centre for Diffraction Data". The specimens were then examined under SEM of Zeiss make. The composition of element present at interface was obtained with the help of EDAX "Energy Dispersive X-rays Spectroscopy". The X-ray dot mapping was used to see the distribution of different element distribution over the interface in these specimens.

4.10 VACUUM LEAK RATE MEASUREMENT IN GLASS-METAL JOINT

After fabricating compression glass-metal seal vacuum leak testing of joint was carried out using "Pfeiffer Vacuum instrument". The experimental set-up of vacuum leak testing is as shown in Figure 4.16. The top surface of the glass tube was ground in polishing machine in order to achieve smooth surface. The joint assembly was then placed over the fixture of instrument. The vacuum in joint was then created with the help of vacuum pump. The leak detection in joint assembly was performed with the help of helium gas.

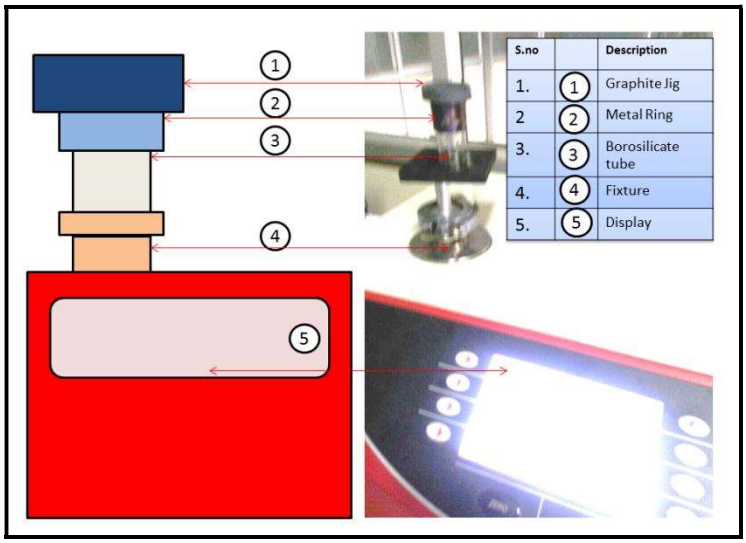


Figure 4.16: Experimental set-up for vacuum leak rate measurement

4.11 IN-SITU WETTING BEHAVIORS OF $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ GLASS SEALANT OVER METAL SPECIMEN

High-temperature image capturing system allows direct in-situ observation of melting and softening behavior of glass over metal substrate [Boccaccini and Hamann 1999]. The change in shape of glass sealant ($40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$) pallet from room temperature to 980 °C was monitored using digital camera along with thermo couple in an induction heating system furnace. The schematic of image capturing system is shown in Figure 4.17, it consists of induction heating set-up, image capturing digital camera, computer, focusing light, infrared thermometer.

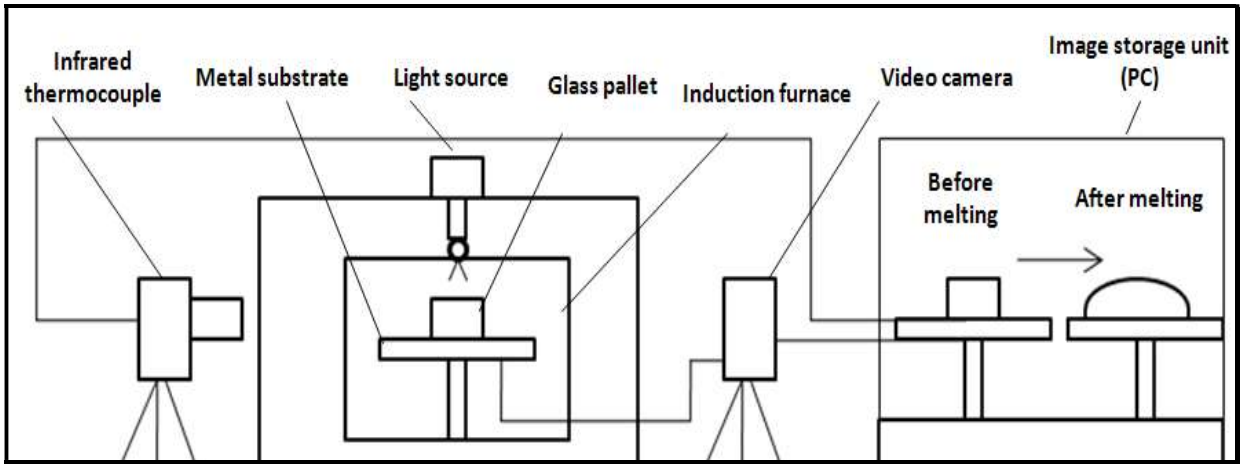


Figure 4.17: A schematic of experimental setup for in-situ wettability measurement

The experimental set-up uses an induction coil, metal strip of SS 304 having dimensions 25 mm × 62.5 mm × 1.5 mm and glass sealant pallet of 8 mm diameter and 10 mm height. The glass sealant pallet was then placed over pre-oxidized SS304 substrate (pre-oxidised at 700°C for 3 minutes) and complete assembly was placed in induction heating system, in order to provide localized heat to metal substrate. Infrared thermometer was installed to measure the temperature of glass-metal assembly. A reference object having known dimension is marked in front screen in order to calculate and correlate image pixel size measured with respect to reference object. The melting behavior of glass sealant pallet at different stages from room temperature to 980 °C was recorded using digital camera. The captured video image was then converted into still image frames. The captured video before melting was converted into still

image and measurement of the initial height of the glass sealant pallet in terms of pixel was carried out using equation given in *(section 4.7page 37).*

4.12 STRUCTURAL INTEGRITY ASSESSMENT OF GLASS-METAL JOINTS

The Structure Integrity Assessment (SIA) of the GMJ was carried out over fabricated GMJ after the estimation of maximum thermal cycling temperature. SIA is an approach to assess whether a glass-metal joint structure is fit to withstand the service conditions safely throughout service. The structural integrity of glass-metal was carried using the two different types of glass-meal joint geometry. In the first case, cylindrical compression glass-metal joint between Austenitic Stainless Steel (SS304) metal and borosilicate glass fabricated. In second case the glass sealant pallet is melted over the surface of SS304 metal specimen. The austenitic stainless steel SS304 was initially machined and thickness of 0.4 mm was obtained using turning and internal boring operation as shown in Figure 4.18 (a). The thickness of metal ring was taken 0.4 mm on the basis of residual stress calculation (Section*4.3.2.1 page 29*). The metal ring after performing machining operation was firstly cleaned with soap solution and then with acetone to remove dust and grease particle from the SS304 metal ring specimen as shown in Figure 4.18 (a). The metal ring specimen was then pre-oxidized in the muffle furnace at 700°C for 3 minutes as shown in Figure 4.18(b). The borosilicate glass tube having dimension 60 mm outer diameter and 3 mm thickness was then cut to 75 mm length and washed with soap solution and acetone as shown in Figure 4.18 (c). The graphite jig was prepared from the cylindrical block having diameter 75 mm and 80 mm height. The graphite jig was then machined in lathe machine using step turning operation. The diameter of graphite jig was reduced to 54 mm diameter and the length of 35 mm as shown in Figure 4.18 (d). The inner surface glass tube was tight fit with graphite jig. The purpose of graphite jig was to align the borosilicate glass tube in the center. The inner diameter of SS304 metal ring was taken slightly larger than the outer diameter of borosilicate glass tube and the space remaining between metal ring and glass tube was filled with glass sealant having composition $40SiO_2$-$54B_2O_3$-$4Na_2O$-$2Al_2O_3$ .The joint was than heated in induction furnace and cooled down to room temperature. The GMJ after cooling to room temperature as shown in Figure 4.18 (e) was subjected to thermal cycling. The joint as shown in Figure 4.18 (e) was heated in muffle furnace.

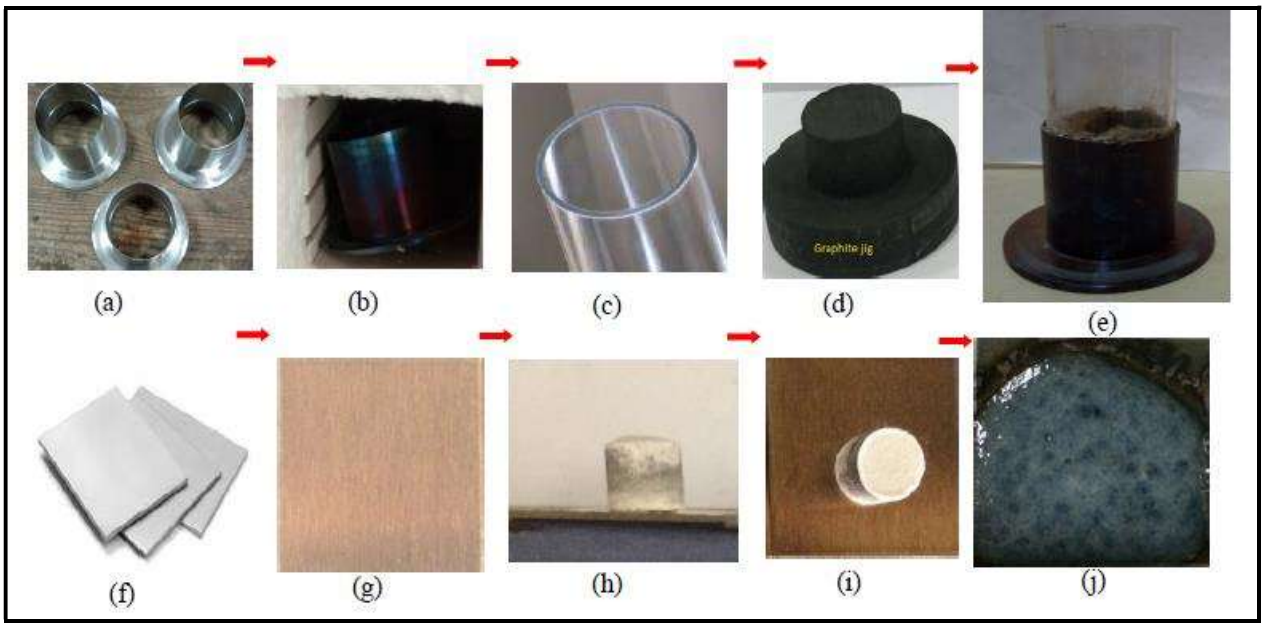


Figure 4.18: Glass-metal joint fabrication process (a) Machined metal ring.(b) Metal ring after pre-oxidation, (c) Borosilicate glass tube, (d) Graphite jig, (e) Glass-metal joint after fabrication, (f) Metal plate, (g) pre-oxidized metal plate, (h) glass pallet, (i) glass sealant pallet placed over the metal specimen, (j) Glass sealant pallet melting over metal specimen.

The (Type2) GMJ fabricated by cutting SS304 from the SS304 metal sheet having dimension (25 mm × 25 mm × 1.5 mm). The metal specimen was then cleaned with soap solution acetone to remove all the dust from the SS304 metal specimen as shown in Figure 4.18 (f). The metal specimen was then pre-oxidized in the muffle furnace at 700°C for 3 minutes as shown in Figure 4.18 (g). The procedure of glass sealant was same as given in (*Section 4.3.2.1.1 page 31*).The fabricated joint subjected to different thermal cycling temperature and different environmental condition is as shown in Table 4.6. The degradation of the glass-metal joint was then examined. The reported in-service operation temperature of glass tube in parabolic trough receiver tube is about 100°C to 170°C [Lei et al., 2012; Espinosa-Rueda.G et al., 2012].

Table 4.6 Design matrix of glass-metal joint for different environmental condition

S.no	Specimen Code	Exposing Environment	Exposure Time	Output Effect
1	GMJ(Type 1)	Heating Furnace (150°C)	50 cycle	Residual Stress
2	GMJ(Type 1)	Heating Furnace (200°C)	50 cycle	Residual Stress
3	GMJ(Type 1)	Heating Furnace (250°C)	50 cycle	Residual Stress
4	GMJ1(Type 2)	Atmosphere	200(hours)	Weight Change
5	GMJ2(Type2)	Water	200(hours)	Weight Change
6	GMJ3(Type 2)	Heating Furnace (150°C)	50 cycle	Weight Change
7	GMJ4(Type 2)	Heating Furnace (200°C)	50 cycle	Weight Change
8	GMJ5(Type 2)	Heating Furnace (250°C)	50 cycle	Weight Change

Therefore, thermal cycling temperature range was selected with minimum 150 °C and maximum 250 °C. The (Type 1) GMJ as shown in Figure 4.18 (e) was subjected to different thermal cycling temperature of 150 °C, 200°C and 250 °C for 50 cycle with heating rate as shown in Figure 4.19. The specimen GMJ1 for atmosphere environment placed in atmosphere and change in weight of specimen was measured in an interval of every 25 hours. The GMJ2 specimen was subjected to water environment and the weight of specimen was measured in an interval of every 25 hours. GMJ3, GMJ4, and GMJ5 specimen were subjected to muffle furnace to provide a heating environment to joint at 150 °C, 200 °C, and 250 °C for 50 cycles each. The change in weight of specimen after each cycle was measured with the help of weighing scale. The specimens GMJ3, GMJ4 and GMJ5 were heated in a muffle furnace.

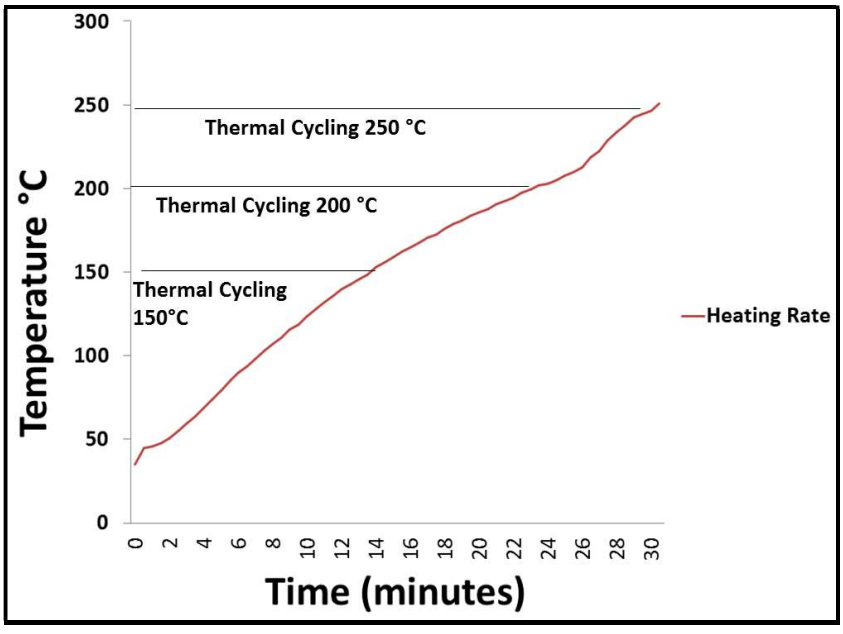


Figure 4.19: Heating curve of compression glass-metal joint specimen for thermal cycling testing

4.13 SUMMARY

The chapter describes the basis for selection of candidate material for the development of glass-metal joint. The various experimental investigations such as wettability study, characterization of oxide formation were carried out before selecting the suitable candidate materials for investigations. The investigation related to glass-metal joint design, residual stress measurements after glass-metal joint fabrication were carried out. The different glass sealants were developed by tailoring the constituent composition and seeing the effect of different constituents on wettability, thermal and structural properties. The in-situ wetting behavior of the selected glass sealant was examined over the metal specimen. The structural integrity assessment of glass-metal joint was carried out after the estimation of maximum thermal cycling temperature.