Review of Literature

2.1 GLASS-METAL JOINING

In the modern era, glasses play a vital role in the fabrication of utensils, optoelectronic material and laboratory instrument. The chemical inertness and high-temperature stability of glass make it a suitable candidate for various applications. Borosilicate glasses are the class of glasses which has been widely known for higher chemical durability, easy formability and for their resistance to heat [Araujo,1980 and 1983; Bouras et al., 2009; Varshneya,1994; Tomsia.A.P, (1993)]. The fabrication of entire structure made up of glass is not possible and the structure must be connected to other metal and alloy [Dobedoe, 1997]. The use of an adhesive for joining glass with metal is an appropriate solution which is valid only for low-temperature applications. Therefore, the joining of glass to metal for high-temperature application is an important issue because of the difference in their structures (glass consists of amorphous structure whereas metal consists of polycrystalline structure) as shown in Figure 2.1 (a) and Figure 2.1 (b).

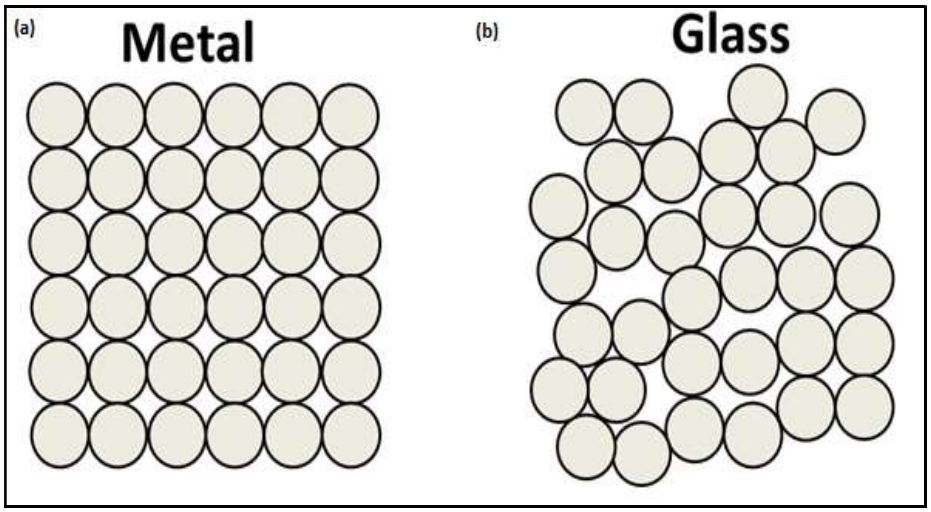


Figure 2.1: Structure of metal and glass: **(a)** crystalline structure of metal : **(b)** amorphous nature of glass

The difference in amorphous and crystalline nature of both glass and metal makes their joining difficult. Glass exhibits brittle behavior whereas metal showing ductile behavior as shown in Figure 2.2.

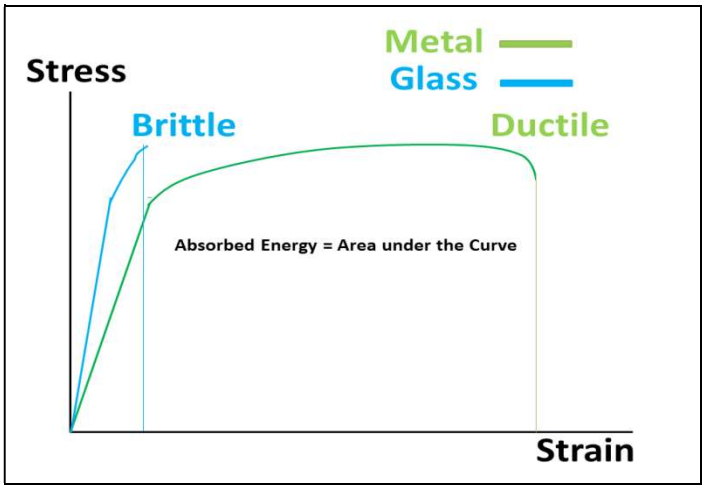


Figure 2.2: Stress-Stain behavior of glass and metal

In spite of having the difference in their structural and mechanical properties, the difference in their coefficient of thermal expansion is also an important consideration which decides the selection of joint geometry. The matched glass-metal joint is used where the coefficient of thermal expansion of both glass and metal is similar. Compression joint is selected where there is a significant difference in coefficient of thermal expansion.

During glass to metal joining process, glass is melted over the pre-oxidized metal surface where glass reacts with an oxide formed after the pre-oxidation process and forms the bond [Donald et al., 2011]. The bonding of SiO_2, takes place with metal M whose surface is coated with an oxide MO as shown in Figure 2.3(a-c). The metal substrate is presumed to be saturated with O and hence in chemical equilibrium with surface oxide.

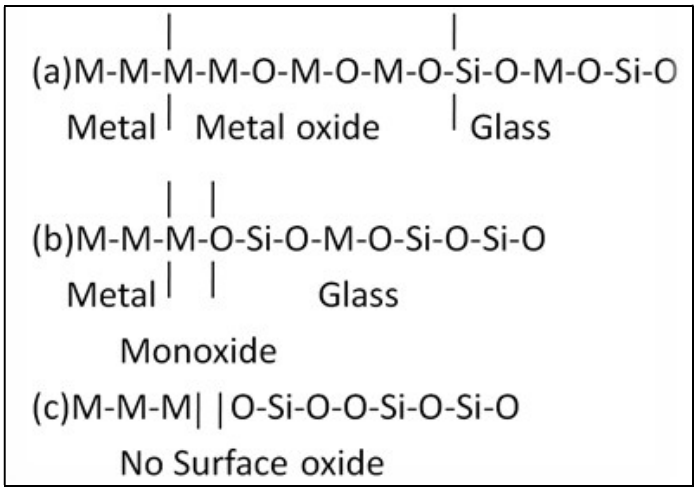


Figure 2.3 Glass-metal joining mechanism: **(a)** with metal oxide layer **(b)** with monoxide layer **(c)** without oxide layer

This in turn is in equilibrium with glass, to produce a local saturation with metal oxide and represented by some M ions in –SiO- sequence. During the joining process, glass is allowed to melt over the metal surface where glass cools with a faster rate as compared to metal because of the supercooling properties of glass. During the cooling process, metal induce stresses on to the glass because of the difference in their coefficient of thermal expansion. In order to make the glass-metal joint of superior quality and to achieve lifetime behavior following requirements must be met.

- Optimum oxide layer thickness must exist at the interface of glass-metal joint [Trajanowski and Zakraysek, 1979]
- The glass should be able to wet and adhere to the metal [Shand and Armistead, 1958]
- The linear expansion of the glass must match closely to that of the metal over a wide range of temperature [Shand and Armistead, 1958]
- The metal should have no thermal critical points (allotropic transformations) within the range of the highest temperatures reached in glass-metal joining process and the lowest temperature reached in service [Shand and Armistead, 1958]
- The glass should neither re-boil when heated for making the seal, nor should the metal give off gases[Shand and Armistead, 1958]

2.2 CLASSIFICATION OF GLASS-METAL JOINT

Based on the coefficient of thermal expansion glass-metal joint, the classification of glass-metal joints is shown in Figure 2.4. Matched type glass-metal joints have similar or nearly matched thermal expansion coefficient for glass and metal components whereas an unmatched glass-metal joint has a significantly different coefficient of thermal expansion for both glass and metal components.

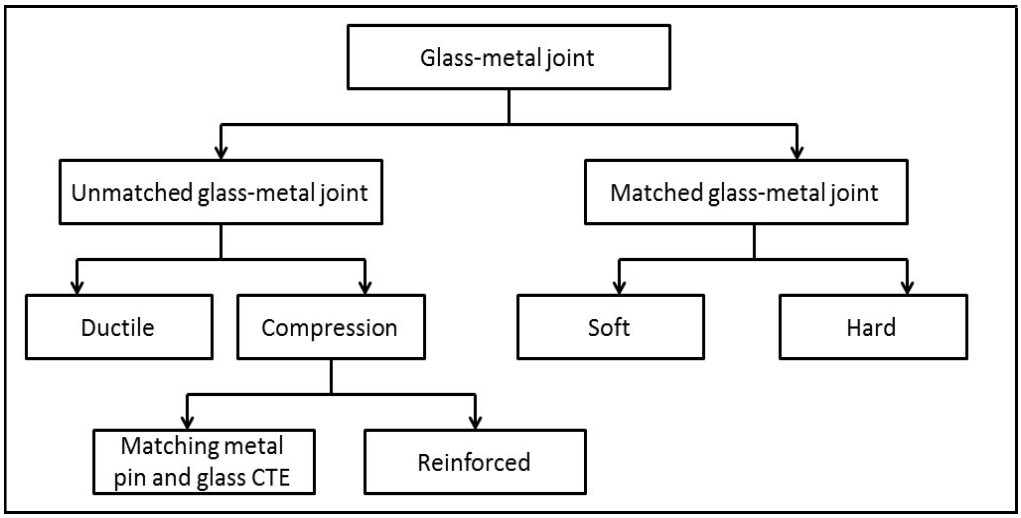


Figure 2.4: Classifications of Glass-metal joints [Jacobs,2007 and Chhibber, 2014]

Matched joints are subdivided depending on the coefficient of thermal expansion of the glass. Hard glasses and soft glasses are classified on the basis of their coefficient of thermal expansion (i.e. Hard glasses have coefficient of thermal expansion is in range 0.5-5.9 x 10^{-6}/℃ whereas soft glasses have coefficient of thermal expansion in the range 6-10.5 x 10^{-6}).
Unmatched types of glass-metal joints can be subdivided into compression and ductile joints as shown in Figure 2.4. Housekeeper joint is the best example of the ductile joint. A common example of a Housekeeper joint is a joint between glass and copper. Copper due to its high ductility is used in housekeeper joint though there is a mismatch in the CTE of copper and glass. The compression joints can be further divided into matched and reinforced compression joints. In the compression joint, the compressive force is generated by the metal envelope on the inner glass containment, the metal used in comparison of the selected glass has considerably higher coefficient of thermal expansion. Reinforced compression joints have a design where a metal pin with the low coefficient of thermal expansion is surrounded by glass having a higher coefficient of thermal expansion and that is further enveloped by a metal containment with the even higher coefficient of thermal expansion. The reinforced compression joints are further subdivided into hard and soft depending on the type of the glass being used for fabrication of glass-metal joint. In the case of a matched joint, the joining is a result of a good chemical bonding at the glass/metal interface between the glass and metal oxide [Jacobs, 2007]. Matching metal pin and glass (CTE) joint are the category of joint where joints can be made of metals, ceramics and glasses having similar coefficient of thermal expansion (The example of matched metal pin and glass (CTE) is Electric feed-through) . In these cases, metal ring is placed outside and glass is filled inside the metal ring. In compression joints, the joint strength is due to the formation of a mechanical bond due to a compressive hoop stress between outer metal and the inner glass portion of the glass-metal joint [Chhibber,2014].

2.3 GLASS-METAL JOINING FABRICATION PROCESSES

The selection of glass-metal joining process is very important for the development of a glass-metal joint. The glass-metal joining requires localized heating of glass just at the interface where it is joined with other metal. In general glass-metal joining techniques are fastening, liquid phase and solid phase joining [Jacobs, 2007; Elrefaeya.A et al.2014; Malfait. W et al.2016]. Fastening is a technique in which fasteners such as screw and nails are used. The use of fastener joins almost any shape or material economically. Adhesive bonding is a type of liquid phase joining where two materials are joined by using an adhesive. The two materials are joined by surface tension force of adhesive in the pores and valleys of two materials. This is the very easy technique to join two materials but is limited up to lower temperature range. Solid phase joining between two materials takes place through diffusion process at an elevated temperature during which one material diffuses over the surface of other material. The glass-metal joint of

cylindrical shape is fabricated using glass blowing technique. In glass blowing operation, glass is melted over the metal specimen and heated locally with the help of flame torch, which contains the mixture of acetylene and oxygen gas. However, the manufacturing of glass-metal joint is not satisfactory using glass blowing lathe operation because of less control in process parameters and higher skilled level of operator is required. The use of high frequency induction furnace for fabricating glass-metal joint is therefore an option for researchers and has been already used in the past [Lei et al., 2012] .

2.4 HISTORICAL DEVELOPMENT OF GLASS-METAL JOINT

The historical development in the area glass-metal joining is shown in Table. 2.1

Table2.1: Historical development in the area of glass-metal joint

S.no	Company name	Location	Historical background	Product	Reference
1.	Heraeus	Heraeus Germany www.heraeus-quarzglas.com	Heraeus, the technology group headquartered in Hanau, Germany, is a leading international family-owned company formed in 1851	Semiconductor Lamp industry Precision- and standard optics, Laser technology, Telecommunications	[Heraeus,(2018)]
2.	Schott	SCHOTT Netherlands www.schott.com	SCHOTT is a leading glass and glass-ceramics group in international level having more than 130 years of outstanding development.	House hold appliances Pharmaceutical industry Solar power collector Automotive industry	[Schott,(2018)]
3.	VTT Technical Research Centre	VTT Technical Research Centre of Finland Finland www.vtt.fi	VTT Technical Research Centre of Finland Ltd is the leading research and technology company from 1942 in the Nordic countries	Embedding optical fibres in metal	[VTT,(2018)]]
4.	UKAEA Culham Special Techniques Group	UKAEA Special Techniques United Kingdom http://www.fusion.org.uk/stg/index.htm	Culham's Special Techniques Group is a highly-skilled material joining facility with more than 40 years of experience as an integral part of the UK nuclear fusion research programme	Ultra-high vacuum Components and Macro/micro-graphic analyses and their experience is an integral part of the UK nuclear fusion research programme.	[CCFE,(2018)]
5.	Panacol	Panacol Germany www.panacol.com	Frankfurt-based Panacol-Elosol GmbH is founded as German subsidiary of Swiss company Panacol AG in 1978	Inorganic adhesive with a temperature resistance up to +1650 UV instrument	[Panacol, (2018),]
6.	Fiber Optic Center	Fiber Optic Center United States of America www.focenter.com	Fiber optics center has been in business since 1991,but in 1982 this was in the name of Boston electronics	Specially fibre Precision glass product Ruggedized optical instrument Spectrometer and accessories	[Focenter,(2018)]
7.	TYDEX	TYDEX Russia www.tydex.ru	Tydex is a private company founded in 1994 in St. Petersburg	spec-troscopy, lasers astro-optics Metrology	[www.tydexoptics.com]
8.	Forschungszentrum Juelich (FZJ)	Forschungszentrum Germany www.fz-juelich.de	The research of Forschungszentrum Juelich is focused on health, information, environment, energy and key competency of physics and scientific computing	They have a lot of experience with brazing and the joining problems in oxide fuel Cells.	[Fzuelich,(2018),]

2.5 APPLICATION OF GLASS-METAL JOINT

2.5.1 Coating Application

The glass-metal joint has been used for various coating applications [Majumdar and Jana 2001; Minghui et al., 2013(a) and (b); Wenbo.L et al., 2013]. The thermal barrier coating protects Ni-based alloys from high operating temperatures using magnesium and Zinc aluminosilicate glass-ceramic [Datta and Das, 2005]. Beside this, glass/ceramic-metal based coating has been used to protect Ti and Ti-based alloy for biomedical applications [Pavon(a,b), 2006; Pavon, et al 2005; Pavon, J et al.2006] as shown in Figure 2.5.

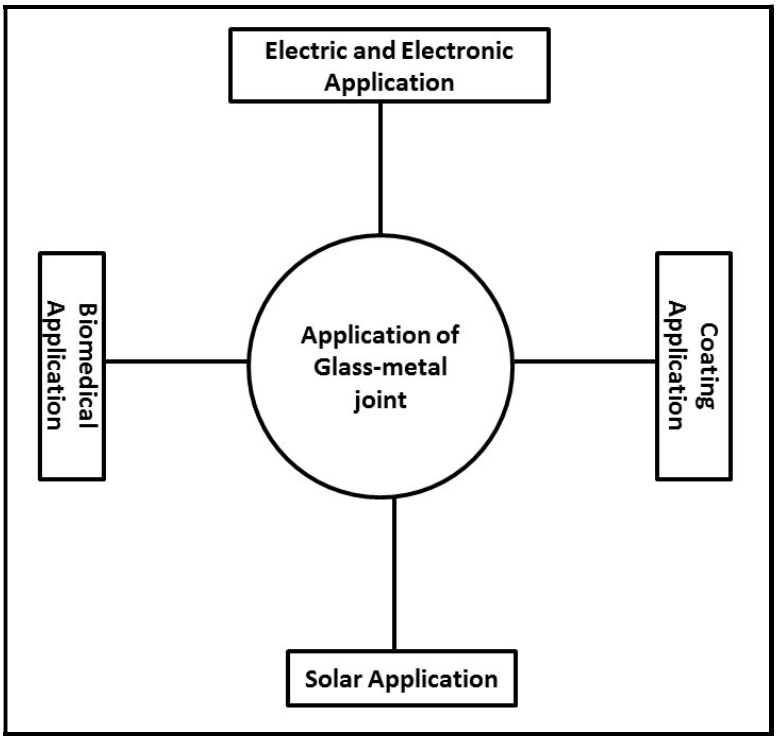


Figure 2.5: Application of glass-metal joining

2.5.2 Electrical and Electronic Application

Glass/ceramic to metal joining has been used for electric feed through, sensor, vacuum valve, and microwave component. The use of an alkali boroalluminosilicate glass with Kovar alloy has been used for the designing of MEMS (Micro-electronic Mechanical system) packaging [Chern and Tsaiv, 2007].

2.5.3 Solid Oxide Fuel Cell

The use of glass-metal joining is increasing day-by-day for the development of solid oxide fuel cell. The use of various austenitic, Ni alloy and ferritic stainless steel has been implemented for the joining of various ($BaO\text{-}Al_2O_3\text{-}SiO_2$) with the addition of various oxides such as B_2O_3, MgO, Na_2O and TiO_2 [Donald et al., 2011].

2.5.4 Solar Application

Glass-metal joint for parabolic trough receiver tube has been reported by Lei et al. [Lei et al., 2011]. The parabolic trough receiver tube is the key component of parabolic trough receiver based concentrated solar power plant. The use of Kodial glass and Kovar alloy glass-metal joint combination has been used for the development of PTRT's [Lei et al., 2010; Lei et al., 2012]

2.6 METAL USED IN GLASS-METAL JOINING

The selection of glass-metal joint combinations purely depends on the application and the requirement. The availability, material cost, coefficient of thermal expansion and thermal stability at elevated temperature are the main factors while selecting the glass-metal joint combination. Some early studies on glass-metal joining have reported the use of the glass-metal joint for various industrial applications as summarized in Table 2.2.

Table 2.2: Application of various glass-metal joint combinations

S.no	Metal	Glass	Application
1.	Fe based alloy ($<3\times10^{-6}$/K over limited temperature ranges for some binary Fe–Ni alloys to $>18\times10^{-6}$/K for some stainless steels.)	Both lithium zinc silicate (LZS) and lithium aluminosilicate (LAS) glass–ceramics	Electric feed through component [Donald, 2007; Donald, 1993]
2.	Nickel-based super alloys cover a more limited thermal expansion range from $<12\times10^{-6}$ /K for Hastelloy B2 to $> 16\times 10^{-6}$ /K for Inconel 718.	lithium zinc silicate glass–ceramic	Glass ceramic coating application [Donald, 2007; Donald, , 1993]
3.	Ti and Ti-based alloys 9.1–9.8 9 10^{-6} /K.	Boroaluminate-based glasses Alkaline earth lanthanum borate glasses	Aerospace engine and airframe part where resistance to chemical corrosion required and biomedical application [Polmear,1995;Jackson 2007 and Brow, 1987]
4.	SS321 stainless steel/Cu pin	LZS glass–ceramic.	Cylindrical seal between stainless steel and copper using LZS ceramic [Goswami , 2007]
5.	Kovar alloys	Kodial glass	Parabolic trough receiver tube application [Lei et al., 2010; Lei et al., 2012]

Based on the literature listed in Table 2.2, it has been concluded that the Fe based alloy, Ni-based alloy, and copper has been used for joining with various glass and ceramic.

2.6.1 Fe Based Alloys

Fe based alloys cover thermal expansion range of $<3\times10^{-6}$/K. In the presence of Ni alloys, this thermal expansion range reaches $>18\times10^{-6}$ for Fe-Ni based alloys. During the fabrication of glass-metal joint, there is diffusion of Fe^{2+} ions that act as glass modifier and are highly soluble and mobile.. The solubility and mobility of Fe^{2+} ions in glass can lead to the formation of diffusion gradient and is responsible for the corresponding variation in thermal expansion within the interface.

2.6.2 Ni-Based Alloys

Ni-based alloys cover more limited thermal expansion range of $<12\times10^{-6}$/K for hastealloys B2 to $<16\times10^{-6}$ for Inconel [Donald et al., 2011]. The variety of Ni-based superalloys have been joined to lithium zinc, silicate-based glass ceramic.

2.6.3 Copper

Melting temperature of copper is approximately 1080 °C and the bonding of copper with glass takes place at 960 °C. Pre-oxidation of copper is not required during the bonding of glass with metal. Due to the oxidation, distortion of copper occurs.

2.7 FABRICATION ISSUES

2.7.1 Wettability

In the process of glass-metal joining the glass wets the surface of the metal substrate, where it reacts with oxide present at the surface of the metal and forms the bond. Wettability can be defined as the tendency of a liquid to spread on the solid surface and is measured in terms of contact angle. Whereas, the extent or degree to which something is spreading is termed as spreadability. Whenever any liquid drop rests on the flat solid horizontal surface then the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface is called contact angle [Cheng et al., 2013]. From young's equation,

$\cos \theta = (\gamma_{sv} - \gamma_{sl})/ \gamma_{lv}$ (1)

Where θ = contact angle

γ_{sv} = Solid/vapor interfacial energy

γ_{sl} = Solid/liquid interfacial energy

γ_{lv} = liquid/vapor interfacial energy

The low value of contact angle (θ) is desirable as interface energy between molten glass and solid surface is low. Wettability of glass over the metal surface is measured in terms of contact angle (θ). The higher value of contact angle leads to lower wettability as shown in Figure 2.6 (c) and Figure 2.6 (a). The contact angle close to 0°, as droplet turns into flat puddle shows good wetting as shown in Figure 2.6(d).

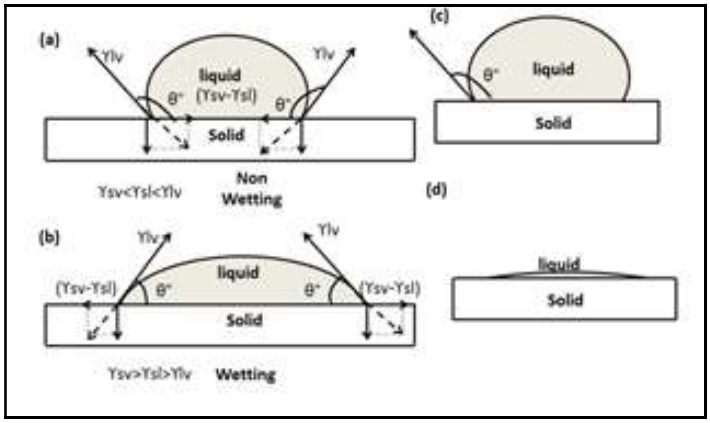


Figure 2.6: Wettability phenomenon in terms of contact angle of liquid drop

Image capturing system, drop size measurements are the common techniques which have been used in the past for contact angle measurement. The factors affecting wettability of glass over the metal surface are the surface roughness, pre-oxidation of metal and types of oxide formed on the metal surface.

2.7.2 Surface Roughness of Metal Specimen

The wetting phenomenon over the plane surface and rough surface is shown in Figure 2.7 (a) and Figure 2.7 (b). The wettability of a material over the surface of material is affected by surface roughness.

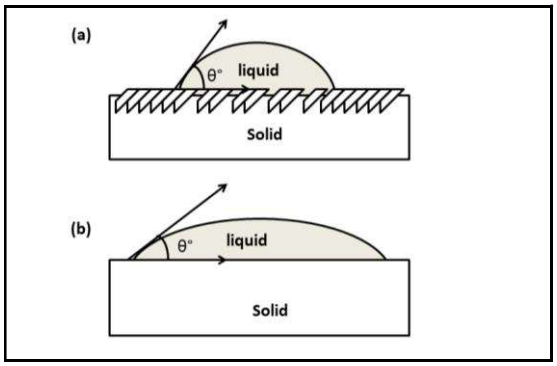


Figure 2.7: Wetting behavior with surface roughness

The wettability studies conducted on much popular material like aluminum, titanium steel revealed that wettability of material over metal substrate depends on thermophysical properties (eg: density, surface tension),as well as on surface roughness [Kubiak et al., 2009]. The surface roughness study on wetting behavior was conducted to understand the wetting behavior of Eutectic Sn-Pb and pure Sn-Cu solder alloy on the copper substrate with different surface finish Viz., highly polished surface, medium polished surface, and unpolished surface with surface roughness range R_a(μm) [0.038-0.178]. The spreading behavior of molten liquid was high at lower surface roughness value R_a(0.038) as compared to higher surface roughness value Ra(0.178) [Nalagtla, 2007].

2.7.3 Pre-oxidation Time and Pre-oxidation Temperature

The bonding of glass to metal was because of the presence of an intermediate layer of oxide. The oxide layer on the surface of the metal was achieved through pre-oxidation of the metal specimen in a controlled environment. Also, the wetting and spreading behavior of silicate glasses over pre-oxidized Kovar alloy was much better than without pre-oxidation of Kovar [Cheng,H et al., 2013]. The wetting and spreading behavior of glass sealant over metal specimen increases as the pre-oxidation temperature increase [Luo and Shen, 2008]. The experimental result of this investigation indicates that pre-oxidation of Kovar alloy for about 10 min at 700 °C provides better adherence of glass with Kovar [Luo and Shen, 2008].

2.7.4 Oxide Layer Mass Gain and Oxide Layer Thickness

The oxide layer formed after pre-oxidation of metal is very important for the development of strong and vacuum-tight glass-metal joint. The low oxide layer thickness results in poor bond formation whereas higher oxide layer thickness causes the metal surface degradation and stress corrosion cracking on the metal surface [Trajanowski and Zakraysek, 1979]. The oxide layer thickness formed on the metal surface was measured in term of oxide layer mass gain and oxide layer thickness. The optimum oxide layer mass gain for joining the borosilicate glass to the Fe-Ni-Co alloy was in the range of $5.9\text{-}8.3\times10^{-4}$ g/cm^2 [Waraporn et al., 2009]. The oxide layer mass gain was measured by measuring the change in weight before and after pre-oxidation divided by the surface area. The oxide layer mass gain (4.635×10^{-4} – 19.93×10^{-4} g/cm^2) also increased as oxide layer thickness increased (52-163 μm) as studied by [Cheng, et al., 2013]. The oxide layer mass gain and oxide layer thickness after pre-oxidation increases as pre-oxidation time and pre-oxidation temperature increase as reported by [Lei et al., 2010].

2.7.5 Types of Oxide Phase Formed after Pre-oxidation

The types of oxide phases formed on the surface of the metal specimen after pre-oxidation depends upon the pre-oxidation time and pre-oxidation temperature. The common types of oxides formed on the surface of metal specimen depend upon Fe/O (Ratio)[Waraporn et al., 2006]. In general, wustite ($Fe_{1-x}O$), magnetite (Fe_3O_4) and hematite (α-Fe_2O_3) types of phases were present after pre-oxidation of Fe based alloy [Luo and Shen 2008]. Wustite (FeO) has a defective halite structure, with anion sites occupied by O^{2-} and most cation sites occupied by divalent Fe^{2+} ions. Cubic close-packed (CCP) array of O^{2-} stacked along the [111] direction is shown in Figure 2.8 (a). Magnetite (Fe_3O_4) has an inverse spinel structure containing both divalent and trivalent iron ions. The distribution of its cation is written as (Fe^{3+}) [Fe^{3+} Fe^{2+}] O_4, where the parentheses denote the tetrahedral sites and the square brackets denote the octahedral sites as shown in Figure 2.8 (b). The crystal system of hematite (α-Fe_2O_3) is a rhombohedral structure as shown in Figure2.8 (c). A study was performed on Kovar alloy and it was concluded that there are three kinds of iron oxides formed on the Kovar surface when it is oxidized at high temperature, which are FeO, Fe_3O_4, and Fe_2O_3 sequentially from internal to the external surface.

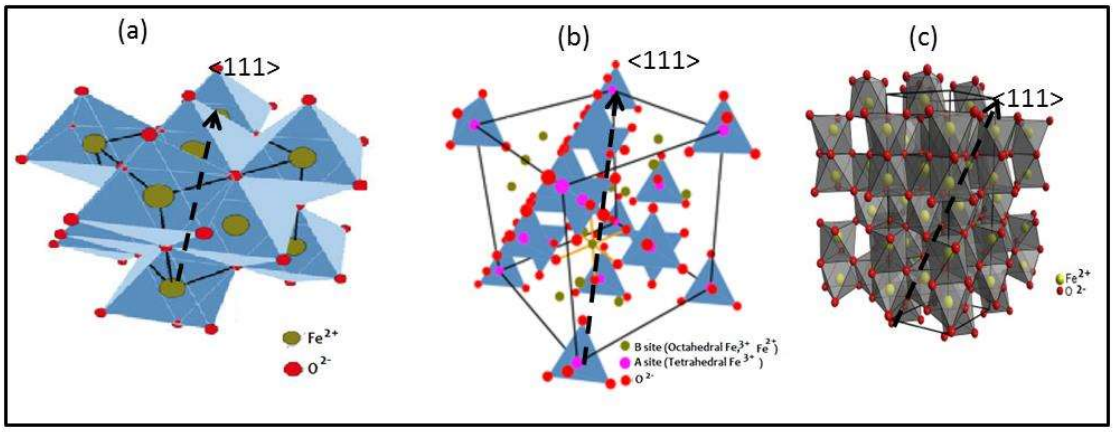


Figure 2.8: Structure of oxide formed after pre-oxidation: (a) FeO, (b) Fe_3O_4, and (c) Fe_2O_3

FeO and Fe_3O_4 oxide phases were considered to be the best oxide formed on the surface of the metal specimen as compared to because of their stable structure as compared to Fe_2O_3 oxide. [Luo and Shen,2008].

2.8 DESIGN OF GLASS-METAL JOINT

The design of glass-metal joint is important from the aspect of reliability and the quality of joint. The glass-metal joint cracks generally at the interface of joint because of the difference in their coefficient of thermal expansion. The selection of glass-metal joint geometry depends upon the coefficient of thermal expansion. Matched type joint design is used where there is a negligible difference in their coefficient of thermal expansion as shown in Figure 2.9 (a). The difference in coefficient of thermal expansion is not recommended for matched glass-metal joint design. The problem of difference in coefficient expansion can be solved using unmatched glass-metal joint (Compression joint design) as shown in Figure 2.9 (b) as reported by [Adam,1954]. The compression glass-metal joint was used where the housing material's coefficient of thermal expansion was greater than that of glass.

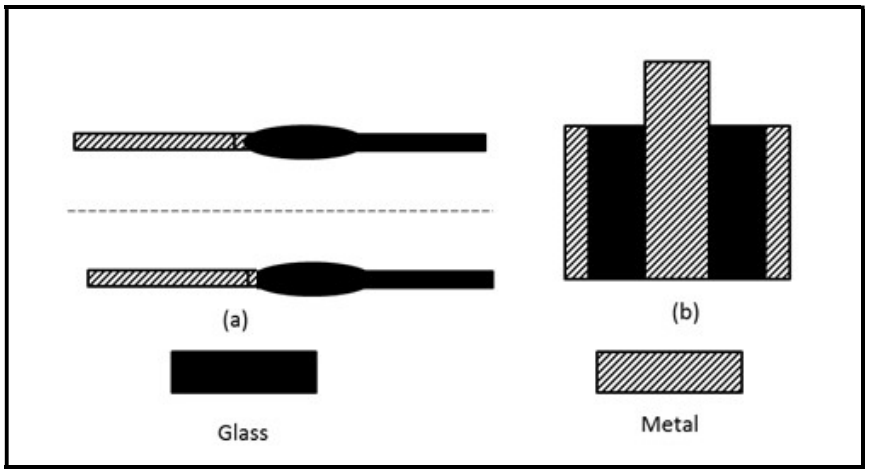


Figure 2.9: (a) Matched and **(b)** unmatched glass-metal joint geometry

The direction of different stresses developed in compression glass metal joint is as shown in Figure 2.10(a-d). During the fabrication process, the metal housing expands during heating as shown in Figure 2.10 (e) and contracts upon solidification which generates favorable homogeneous compressive radial stress on the glass at the interface as shown in Figure 2.10(e). These compressive stresses generated in glass-metal joint interface made this joint to withstand high pressure, physical stress, and thermal shock as compared to matched joint. The glass endures maximum stresses in compression than in tensile loading.

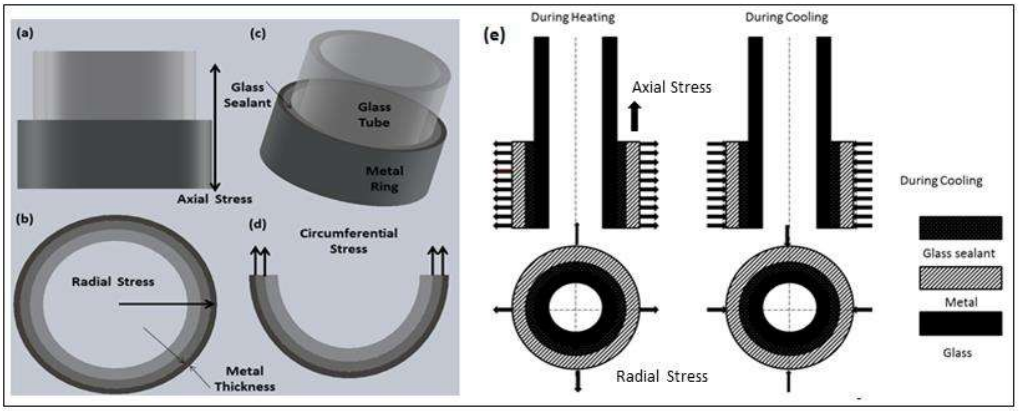


Figure 2.10 : (a-d) The direction of different stresses in compression glass metal joint, (e) Stresses generated in compression glass metal joint during heating and cooling

The strength and adhesion of metal with glass depends upon the selection of glass sealant during the joining of glass with metal. The wettability and strength of compression glass-metal joint depends upon the various factors such as glass sealant selection, metal ring thickness, residual stress generation, thermal cycling and interfacial reaction between glass and metal substrates.

2.9 SELECTION OF GLASS SEALANT

The main criteria of selecting glass sealant are glass transition temperature T_g and coefficient of thermal expansion. Glass sealant wettability must be as high as possible because higher wettability confirms superior bonding of sealant with the metal substrate. Glass sealant must show adequate viscosity behaviour to enable joining by softening. The higher viscosity of the glass sealant would reduce wettability and lower viscosity would cause in sealant to flow out. The glass sealant transition temperature and softening temperature are the parameters which predict the flow of glass sealant. The (T_g) glass transition temperature and (T_s) softening temperature of glass sealant depends upon the chemical composition of glass sealant. The following requirements must be met before designing compression glass-metal joint.

- The glass transition temperature Tg and crystallization temperature Tc of glass sealant must be less than those of borosilicate glass tube otherwise glass tube will melt before borosilicate glass tube.
- The density of glass sealant must be as high as possible.
- The percentage weight loss with respect to temperature must be as low as possible. Low percentage weight loss is responsible for the higher stability of glass sealant.
- The spreading behaviour of glass sealant over metal specimen must be higher whereas contact angle formed by glass sealant must be as low as possible because low value of contact angle confirms higher wettability.
- The thermal conductivity of glass sealant should be lower. The higher thermal conductivity of glass sealant would transfer maximum heat to the glass tube.

The various glass sealant compositions along with their glass transition temperature are shown in Table 2.3.

Table 2.3: Various glass sealants and their chemical composition used in glass-metal joining

Composition (Mol %)						Glass transition Tg	Reference
SiO_2	B_2O_3	Al_2O_3	Alkali earth		Other		
			BaO/SrO	CaO/MgO			
Boroaluminosilicates							
30	15	10	40 BaO		5 La_2O_3	667	[Anderson and Tietz,2003]
38	12	10	35 BaO		5 La_2O_3	739	
33	17	10	35 BaO		5 La_2O_3	678	
29	21	10	35 BaO		5 La_2O_3	652	
33	17	10	35 BaO		5 La_2O_3	656	
30	22	10	36 BaO		2 ZrO_2	614	
34	17	10	36 BaO		3NiO	617	
Borosilicate							
32	2	0	40 BaO	10 CaO	16	660	[Steel and Heinzel, 2001]
33	3	0	40 BaO	10 CaO	14	662	
31	8	0	38 BaO	15 CaO	8	626	
34	8	0	42 BaO	8 CaO	8	623	
30	7	0	37 BaO	16 CaO	10	630	
Aluminosilicates							
50	0	5	45 BaO			730	
Borate							
8	40	7	25SrO		20 La_2O_3	760	[Minh,1993]

The various types of glass sealant which have been used in glass-metal joining application are given in Table 2.4.

Table 2.4: Various glass compositions used in the past for various application [Donald et al., 2011]

Glass code	Composition (mass %)												Reference
	Li_2O	Na_2O	K_2O	MgO	CaO	BaO	ZnO	B_2O_3	Al_2O_3	SiO_2	P_2O_5	Other	
Titanium metal Coating(Ti l)	-	6-14	-	-	22-26	-	-	-	4-9	50-58	-		[Brow and Watkins, 1987]
Calcium Boro-aluminate Glass-12 (CABAL-12)	-	-	-	-	15.9	-	-	43.8	28.9	-	-		[Sharma et al., 2004]
Calcium Boro-aluminate Glass-17(CABAL-17)	-	-	-	-	40.5	-	-	30.1	29.4	-	-		[Donald et al., 2011]
Barium Boro-aluminate Glass-17 (CABAL-17)BABAL-12	-	-	-	-	-	43.9	-	26.6	9.7	-	-	19.8Sro	[Sharma, et al., 2004]
Corning Glass 0080 (0080)	-	17.0	-	4.0	5.0	-	-	-	1.0	73	-		[Sharma, et al., 2004]
Titanium metal alkali barium silicate glass (TM-9)	-	7.8	5.2	-	-	6.3	-	-	2.6	78.1	-		[Sharma, et al., 2004]
Lithium zinc silicate high ZnO (LZSH)	8.88	5.42	-	-	-	-	24.05	5.0	-	53.70	2.95		[Donald et al., 2011]
Lithium zinc silicate low ZnO (LZSL)	12.65	-	2.95	-	-	-	1.85	1.2	3.6	74.4	3.15		[Donald et al., 2011]
Bioglass (B Glass)		24.5	-	-	24.5	-	-	-	-	45	6		[Donald et al., 2011]
Borophosphosilicate (BPS)	13.4	-	2.9	-	-	-	2.0	1.1	3.7	74.1	2.8		[Donald et al., 2011]
Sandia S-Glass	12.6	-	4.9	-	-	-	-	3.2	5.1	71.7	2.5		Ley et al., 1996

2.10 VARIOUS FACTORS AFFECTING GLASS SEALANT

2.10.1 Sio_2/B_2o_3 Ratio

Most of the glass sealant contains SiO_2 and B_2O_3 as main glass constituent. Studies carried by researchers [Tian,Y. et al., 1996] on glasses have shown that the ratio of SiO_2/B_2O_3 is the dominant factor to tailor the glass transition temperature and viscosity of glass sealant. Glass sealants with lower SiO_2/B_2O_3 ratio exhibit lower glass transition temperature Tg. The formation of boron oxygen triangle by B_2O_3 deteriorates the strength of basic tetrahedral Si-O glass network which causes the decrease in the viscosity and wettability of glass sealant over the metal substrate. Moreover, the effect of the ratio of SiO_2 to B_2O_3 on the glass properties was explored by [Jean-Barnerd Bouche,(2009)] and have shown that as the SiO_2 to B_2O_3 ratio in the glass increased from 4.18 to 5.77, the thermal expansion coefficient decreases from 4.95×10^{-6}/ ℃ to 4.55×10^{-6}/℃. The increase in coefficient of thermal expansion decreases the glass transition temperature Tg.

2.10.2 Effect of Additive Addition

Other than SiO_2/B_2O_3 ratio, several other additives are also available which are used to tailor the properties of glass sealant. However, the choice of additive not only affects just one property but simultaneously affects the other properties also. The effects of various glass constituents on the glass sealant are listed in Table 2.5.

Table 2.5: Effect of glass constituent on glass sealant properties [Jean, 2009; Donald et al., 2011]

Additive	Effect on glass sealant properties
B_2O_3	Reduce glass transition temperature and increases wettability
Na_2O	Increases conductivity
La_2O_3, Nd_2O_3, Y_2O_3	Increase melting ,glass transition temperature
P_2O_5	Improve flux
Al_2O_3	Improve the flux and decrease thermal expansion coefficient
TiO_2	Stimulate crystallization
CaO	Increases strength and glass transition temperature
MgO	Stimulates crystallization
BaO	Increase coefficient of thermal expansion

The addition of Al_2O_3 in glass system improves fluxing and improves joining behavior but on the other hand, the excess addition of Al_2O_3 in glass system decreases the coefficient of thermal expansion and promotes the formation of crystallization phase. The decrease in the coefficient of thermal expansion of glass sealant results in an increase in the glass transition temperature and the decrease of wettability over metal.

2.11 DESIGN OF GLASS SEALANT COMPOSITION

The constituent of glass sealants play important role on their properties during the designing of glass sealant composition. The constituent with their effects on the properties of glass sealant listed in Table.2.5. However, the full understanding of the relation between each glass constituent and its significant properties is difficult to achieve. The statistical design of experiments approach has been used by [Taguchi, 1987] in order to obtain the effect of individual glass sealant constituent on its output response by using sets of significant factors. The statistical design of experiments for the development of glass sealant for Solid Oxide Fuel

Cell (SOFC) has been studied by some researchers [Jean, 2009]. During experimentation, the chemical composition of SiO_2, BaO and CaO were varied while taking Al_2O_3 as 2.5 wt%. The full factorial model was implemented on these three independent parameters on at least $(2^3+1) = 9$ compositions, of the glass. The range of glass sealant constituents was selected on the basis of a phase diagram of three component system.

2.12 RESIDUAL STRESSES

The residual stresses are the stresses which remain in the material without the application of external force. These stresses are inevitable in the glass-metal joint as a result of the difference in coefficient of thermal expansion of glass and metal, when it gets cooled down from the joining temperature to the room temperature. These stresses result in the decrease of the joint strength and reliability of glass-metal joint. Other than the coefficient of thermal expansion, the intensity of residual stress also depends upon the design geometry, the thickness of metal ring as well as the thickness of glass tube [Dongqiang et al., 2007; Hull and Burger 1934]. A study conducted on glass-metal joint used in parabolic trough receiver tube by [Dongqiang et al.,2007] reported that the most detrimental stresses developed in glass-metal joint are axial stresses which act near the joint interface on the outer surface of the glass tube . The study also concluded that the thickness of metal ring should be as thin as possible. The joint strength of glass metal joint increases as thickness of glass tube increases. In another study reported by [Shekoofa et al., 2014] the best shape of the metal cross-section is trapezoidal which leads to lower level of residual stress at the interface of the glass-metal joint. The residual stresses generated inside the glass tube was measured with the help of photo-elastic technique reported by [Aden.H et al.,2008].

2.13 INTERFACIAL REACTION

The bonding in glass-metal joint depends upon the interface characteristics. The interfacial reaction between the diffusing metallic species and the glass constituent including the nucleating agent employed for specific glass ceramic system must be avoided [Donald, 2007 and McMillan, 1979]. During the joining of glass containing P_2O_5 with metal, the undesirable reaction between metallic alloy Fe or Cr with P_2O_5 glass system leads to the formation of iron and / or chromium phosphate precipitation at the interface

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$$22(Cr/Fe) + 3P_2O_5 - 6(Cr/Fe)_2P + 5(Cr/Fe)_2O_3$$

$$9(Cr/Fe) + P_2O_5 - 2(Cr/Fe)_2P + 5(Cr/Fe)O$$

2.14 STRUCTURAL INTEGRITY ASSESSMENT

Structural integrity assessment (SIA) of glass-metal joining is an evaluation and an investigation of integrity and worthiness of joint. The glass-metal joint is subjected to different cyclic loading condition during in service operation over the period of time. In case of glass-metal joint for parabolic trough receiver tube application, the joint is subjected to thermal cycling conditions of heating during day and cooling at night. This cyclic heating and cooling of plant leads to the formation of residual stress in the glass-metal interface. The generated residual stresses in the joint interface crack the glass tube at the interface which decreases the level of vacuum inside the tube and also its performance [Shekoofa et al., 2014]. Other than parabolic trough receiver tube all electronic feed though and glass-metal sealing components are also subjected to thermal cycling condition and the performance of the component is affected over the period of time.

2.14.1 Thermal Cycling

In order to attain hermitic glass-metal joint the residual stresses generated after the thermal cycling must be as low as possible and must be compressive in nature [Lei et al., 2010]. During the heating of glass-metal joint assembly both glass and metal expands according to their coefficient of thermal expansion and starts contracting during cooling. As glass is super cooled liquid which cools faster than metal so metal starts producing stress in glass and breaks the glass, if stress is exceeded above the endurance limit of glass. In case of parabolic trough receiver tube, entire tube subjected under the sun is heated during day time and cools during night time. This heating and cooling of tube during day and night service in operation produce stresses at the interface and cracking of glass tube at joint interface occurs. The cracking of glass tube leads to the loss of vacuum in the tube and as a result of vacuum loss the thermal efficiency of tube decreases during service.

2.14.2 Environmental Degradation

Corrosion on the surface of metal appear due to environmental conditions (temperature and humidity), over the period of time [Greiner and Stoch, 1996]. The chemical reaction between glasses and environmental oxide causes the deteriorations of material or object [Camuffo, 1992].

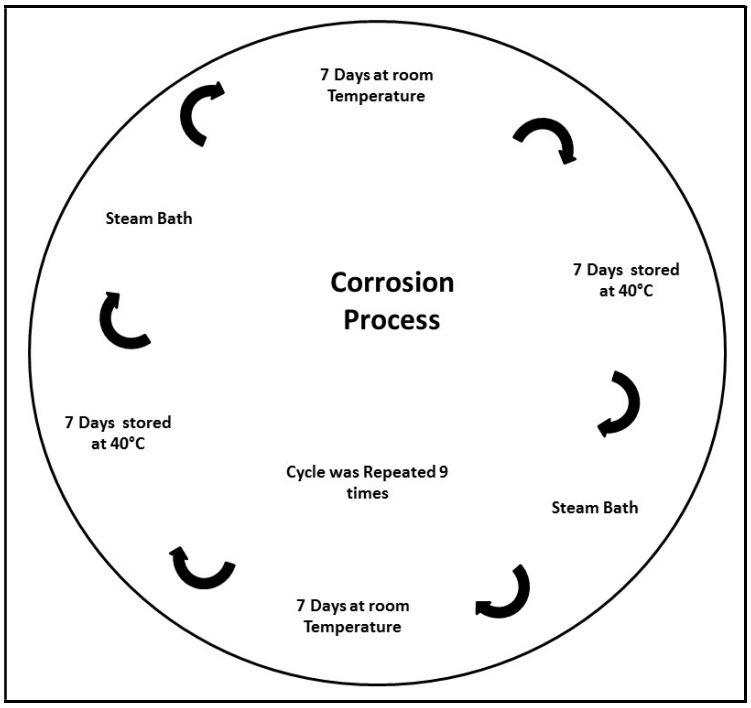


Figure 2.11: Graphical scheme of induced corrosion in glass-metal joint

In many applications, glass-metal joint is used, and the presence of environmental conditions deteriorates the quality of the glass-metal joint. The mechanism of corrosion of glass such as glass crystallization was discussed by [Hench, 1975] and glass corrosion is primarily a result of hydrolysis and leaching [Colomban,2008)]. The process of corrosion starts first from the metal side and then it moves to the interface of glass-metal, where it decreases the bonding strength at the interface of joint. To study the surface change on glass sensor, an artificial corrosion process was induced by selecting various corrosive agents such as hydrochloric acid, sulfuric acid, water and formaldehyde. The graphical scheme of inducing corrosion in glass-metal joint of glass sensor is shown in Figure 2.11. In induced corrosion process, specimen was kept in room temperature for 7 days and then at 40°C for next 7 days. The specimen was then subjected to steam bath and again kept at room temperature for next 7 days and again at 40°C for next 7 days after steam bath. The cycle was repeated 9 times to induce corrosion on glass/metal joint assembly.

2.15 SPECIFIC LITERATURE REVIEW

The aim of present work was to study the glass-metal joint for the parabolic trough receiver tube (PTRT) as shown in Figure 2.12(a). The performance of concentrated solar power plant is directly influenced by the working of parabolic trough receiver tube as reported by Henry Price et al and V.K.Jebasingh et al [Jebasingh and Joseli 2016; Price et al. 2006]. The PTRT covers 20% of the total cost of any solar thermal power plant [Price and Kearney 1999].

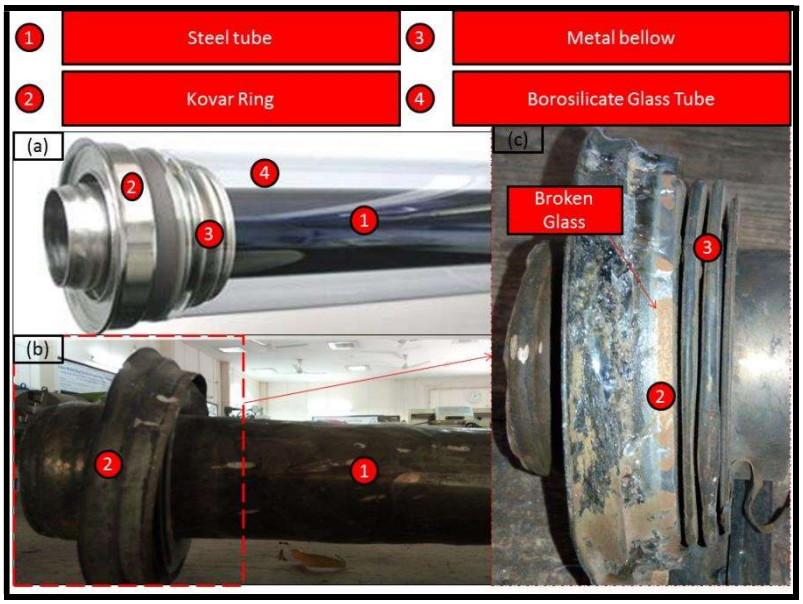
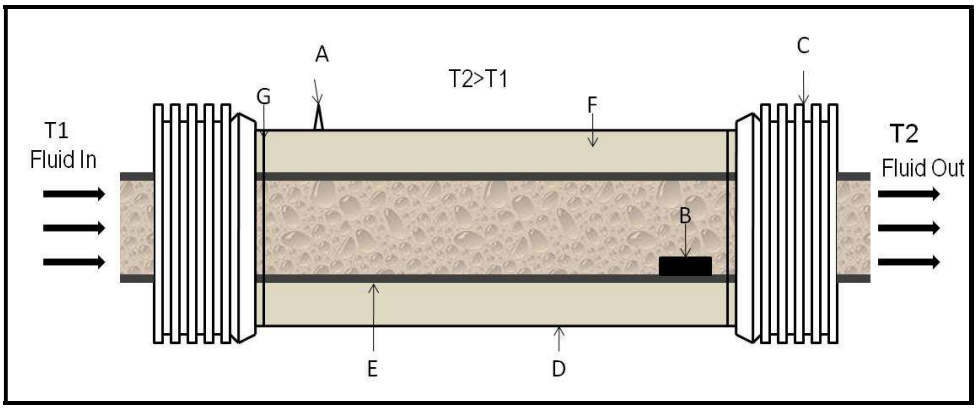


Figure 2.12 : (a) Parabolic trough receiver tube, (b) Glass broken receiver tube, (c) Enlarged view of glass-metal joint Interface

In the survey of 9 solar thermal power plants in the USA, the failure rate of PTRT was about 30-40% over the time period of 9 to 11 years of operation [Lei et al., 2010]. The failure of these PTRTs takes place chiefly because of thermal stresses at the glass-metal interface which causes loss of vacuum, degradation of solar selective coating and fracture of glass tube, as shown in Figure 2.12 (b). In power plants, all the receiver tubes are joined in series to form a loop and the cost of replacement of the damaged glass tube is around 1000 USD. For replacing a single broken tube, the complete loop needs to be shut down, which affects the cost and efficiency of the entire power plant [Mahoney,2000; Lei et al., 2010]. The enlarged view of the damaged tube at the glass-metal joint interface is shown in Figure 2.12 (c).

PTRTs comprise of a central metal pipe coated with solar selective coating surrounded by glass tube as shown in Figure 2.13. The two ends of the glass tube are joined with metal ring and are further connected to the metal bellow to accommodate expansion arising during in-service operation. The space between the glass tube and metal pipe is evacuated to around 10^{-3} mbar vacuum level [Lei, D et al.2010]. The vacuum enclosure between metal pipe and glass tube helps to reduce heat loss and protect the surface of metal pipe from oxidation at higher operating temperature.



A: Evacuation Tube B: chemical sponges (Getters) to maintain and indicates the status of vacuum. C: Bellow. D: Glass envelops. E: Steel absorber tube. F: vacuum between the glass and metal tube. G: Glass to metal joint.T_1: Fluid inlet temperature.T_2: Fluid outlet temperature

Figure 2.13: The geometry of parabolic trough receiver tube

In the glass-metal joining of glass and metal, glass is melted over the metal surface and reacts to form an interface. The bonding of glass with metal mainly depends upon the type of oxides present in the metal surface after pre-oxidation. The oxides formed on metal surface after pre-oxidation acts as bonding agent at the interface between the glass and the metal. The properties and types of oxides formed at the interface affect the bonding of the glass with the metal. Other than oxide phase formed after pre-oxidation, the role of residual stresses in glass tube is, therefore, an important issue. The intensity of residual stresses generated depends upon the thickness of metal ring. The decrease in metal ring thickness reduces the intensity of residual stresses [Lei et al.2010]. The thermal expansion mismatch between glass and metal is another important factor for the development of the glass-metal joint. Compression joint geometry is used where there is large difference in coefficient of thermal expansion that appears between glass and metal. The assessment of structural integrity of any component is an evolution and investigation of any component for its safe and reliable operation over the period of time. During the investigation, the component was subjected to various known loading conditions and its behavior was examined. The examination of structural integrity assessments of the glass-metal joint is, therefore, an important and critical issue. The PTRT was subjected to environmental condition during day and night time, which causes PTRT to withstand thermal cycling condition results in the degradation of glass-metal joint over the period of time.

2.16 Summary

This chapter reviews the importance of glass-metal joining. The requirements for achieving a glass-metal joint of superior quality have been described. The classification of glass-metal joints and the use of different processes for joining have been detailed. The historical development of glass-metal joint and its various applications have been summarized. The fabrication and design issues accompanying the development of glass-metal joint have been explained. The specific literature reviews shows the research being carried out for the development of glass-metal joint for the parabolic trough receiver tube applications.