Some developments on ceramic-to-metal and glass-ceramics-to-metal seals and related studies

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Abstract
Seals and coatings based on ceramics and glass-ceramics find numerous applications in different disciplines of science and technology including space, accelerators, nuclear energy, chemical industry. Ceramic-to-metal (CM) seals based on conventional design (using brazing alloys) and glass-ceramics have been prepared. While Ag-Cu brazing alloy has been used in conventional CM seal, we have employed lithium zinc silicate (LZS) and lithium aluminum silicate (LAS) glass-ceramics for glass-ceramics-to-metal (GCM) seals. LZS glass-ceramics based on two different compositions; (a) LZSL composition (wt.%)- Li$_2$O: 12.65, ZnO: 1.85, SiO$_2$: 74.4, Al$_2$O$_3$: 3.8, K$_2$O: 2.95, P$_2$O$_5$: 3.15, and B$_2$O$_3$: 1.2 (low ZnO) and (b) LZSH composition (wt.%)- Li$_2$O: 8.9, ZnO: 24.03, SiO$_2$: 53.7, Na$_2$O: 5.42, P$_2$O$_5$: 2.95, and B$_2$O$_3$: 5.0 (high ZnO) were prepared with desired sealing characteristics for matched type seals. In addition, (wt.%) 12.6Li$_2$O-71.7SiO$_2$-5.1Al$_2$O$_3$-4.9K$_2$O-3.2B$_2$O$_3$-2.5P$_2$O$_5$ (LAS-GC) was investigated for compressive type of seal. LZS glass-ceramics-to-Cu as well as SS-321 seals were found to withstand a vacuum of $10^{-6}$ Torr with leak rate $10^{-9}$ Torr l/s and LAS GC-to-SS304 seal showed high pressure endurance of 12000psi. In order to understand the mechanism of sealing, glass-ceramics-to-metal interface study has also been carried out.

I. Introduction
Seals and coating based on glass/ceramic/glass-ceramic-to-metal/alloy (GM/CM/GCM) have very important role in many technological applications such as feed through in UHV systems, encapsulation for various electrical, electronic and opto-electronic devices (e.g. resistors, capacitors, detectors, etc.), plasma and electron tubes etc. [1-4]. The important parameters related to those seals and coatings are insulation resistance, flash over voltage, current carrying capacity, hermeticity, operating temperature and pressure load capacity, mechanical strength, corrosion resistance, solderability etc. [5-9]. The joints/seals provide an interface between two extreme atmospheres for carrying out a desired and controlled experiments/function. The main requirement for the formation of a high quality seal is to achieve ideal bonding structure at the interface of the metal and ceramic/glass-ceramics part. In above condition, bonding of such ceramics and metals with different thermal expansion coefficients (TEC) can be a problem, especially when heat is applied. In addition, thermal shock, loss of hermetic sealing and increase in corrosion susceptibility at the metal/ceramic/glass-ceramics interface are areas of concern. To avoid such undesired properties thermal expansion coefficients of both the metal/alloy and ceramic should match as closely as possible to minimize the stresses at the interfaces.
Depending on thermal expansion coefficient of metal, hermetic glass-to-metal seal (gas tight seal) are of two types, (1) matched type (TEC of metal ~ sealing material), and (2) compressive type of seal (TEC of metal housing> sealing glass material). Similarly we have three types of ceramic-to-metal seals: (i) conventional ceramic-to-metal seal, (ii) active alloy brazed-CM seal and (iii) glass-ceramic-to-metal seal. For conventional ceramics-to-metal seals we use an intermediate solder/brazing alloy for establishing bonding between metallized ceramic (e.g. pure Al₂O₃) and metal. Among others, in case of alumina the moly–manganese process is widely used to metallize the surface, after plating with nickel the metallized alumina are then soldered or brazed to the Kovar/SS alloys in a furnace with a controlled reducing atmosphere. Well brazed joints are obtained consistently by proper adjustment of temperature, time, atmosphere and fixturing. For active alloy brazing technique metallization of ceramic is not required. The ceramic directly bonds metal in presence of active brazing alloy. Whereas, glass-ceramics–to-metal seals are rather new and offer a number of advantages such as better chemical durability, mechanical strength and tailoring of expansion coefficients nearly matching to those of variety of metals [7-9]. Hence glass-ceramics can also directly bond to the metal/ alloy under suitable conditions. Controlled crystallisation and resulting microstructure in glass-ceramic result seals and coatings of superior mechanical, thermal, corrosion resistance and other properties compared to the glasses/ceramics. In addition we get the greater range of practical thermal expansion coefficients with glass-ceramics, allowing the formation of well matched seals. This can be achieved by careful selection of starting glass composition, nucleants, and the heat treatment schedule employed to crystallise the glass so that specific crystalline phases are formed.

The properties of ceramic components with respect to temperature, resistance, inertness, and mechanical strength increased the possibility of miniaturization chemical industry, microelectronics and components in energy systems. In order to form a mechanically strong, adherent hermetic seal or coating to a metal, formation of chemical bond at the interface between ceramics and the metal is essential. The design of the seal depends upon the size, application, precision required by the end use. Brazing is the most effective and widely used technique for joining ceramics, such as pure Al₂O₃, Si₃N₄ to metals.

Different glasses and glass-ceramics based on silicates, borates, phosphates have been reported for synthesizing the glass-ceramics suitable for sealing/coating [10-14]. We have studied different glasses/glass-ceramics with requisite thermal expansion and wetting characteristics for fabrication for hermetic seals with different metals/alloys. Some of these are, SiO₂-Na₂O-K₂O-Al₂O₃-B₂O₃ (BS) for matched type of seal fabrication with Kovar alloys [15], SiO₂-Na₂O-K₂O-BaO-PbO for fabrication of compressive type of seals with SS 446 and stainless steel [16], P₂O₅-Na₂O-B₂O₃-BaO-PbO (LS) for fabrication of matched type of seal with low melting metals/alloys like Al/Cu-Be [17], Li₂O-ZnO-SiO₂-P₂O₅-B₂O₃-Na₂O (LZS) glass-ceramics to fabricate matched type of seals with Cu and SS 321[18,9] and Li₂O-Al₂O₃-SiO₂-K₂O-B₂O₃-P₂O₅ (LAS) for compressive seal with SS 304. We have also prepared Ni and Cu doped LZS glass-ceramics for multi pin hermetic seals with SS 321. In this paper we will discuss the development of these CM and GCM seals and related aspects.

2. Bonding mechanism
Glass/ceramics/glass-ceramics-to-metal adherence involves the wetting of glass/ceramics/glass-ceramics on the metal/ alloy surface and subsequent chemical reactions and mechanical bonding. Generally, the wettability is assessed by the contact angle. A glass-to-metal contact angle of less than 90 indicates good wetting; while that exceeding 90. implies poor wettability. A small contact angle would mean less surface tension, thereby resulting better the wettability [19-22]. Preoxidation of metal/alloys is very important to produce a thin and adherent oxide layer on the surface of the metal/alloy. It is generally done by heat treatment at different temperatures and isothermal holding periods depending upon the metal/alloys. Previous studies have reported that the optimum thickness of this layer for achieving high-quality junction is 2–10µm [23]. Wetting at the interface indicates adhesion of glass to the alloy surface, which will facilitate sealing and joining. Different theories are
proposed for bonding of metal and glass/glass-ceramics [10]. Among them, mechanical bonding are based on dendrite and electrolytic theories whereas, chemical bonding is accomplished by a transition zone in which the metallic bonding of the metal is gradually substituted for the ionic-covalent bonding of the glass. It is well understood that good bonding always occurred when the glass is saturated with appropriate metal oxide. It is suggested that when appropriate metal oxide is dissolved in the glass up to saturation, metal ions will remain at the surface and these will promote metal to metal bonding across the interface. However, it is also important to prevent chemical reactions providing undesirable reaction products leading formation of highly localised internal stress.

3. Preparation of seals
Broadly seal fabrication involves preparation of metal parts, preparation of glass/ceramics/glass-ceramics parts, their assembly in desired fashion, loading in a controlled ambient furnace, seal formation by melting glass/brazing alloy/ceramisation and annealing. The seals are cleaned and subjected to desired acceptances tests such as insulation, vacuum tightness, high pressure, temperature and voltage endurance, mechanical strength, corrosion resistance etc. A typical schematic assembly of suitably/designed graphite jig, metal housing, metal pins, glass perform is shown in Fig.1. Hermeticity of a seal is checked on a helium leak detector. Depending on the application, high pressure (upto 12-15 kpsi), thermal cycling, mechanical (vibration) tests are also performed on appropriate instruments/systems.

![Fig. 1 Schematic of seal fabrication assembly.](image)

3.1 Ceramic-to-metal (CM) seals
As the thermal expansion characteristic of ceramics and metal are different we need an intermediate material which can accommodate the mismatch and provide good wettability to the surface to bind them. In one of the procedures for fabrication of CM seal, metallization of ceramic component (usually high alumina tube) at the sealing place is done by applying hot metallizing solution (mixture of \( \approx 90\% (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \) and 10\% KMnO_4) on preheated alumina followed by heat treatment in flowing H_2 at 1000°C. A proper balance between the formation of MnAl_2O_4 and Mn-Mo alloy occurs under moist hydrogen to yield well adherent conducting coating. Once alumina becomes conducting it is nickel plated (8-10µm) to have good adherent coating for brazing followed by sintering in H_2 atmosphere. The sintered nickel-plated and metallized alumina tube is then brazed to the metal part using the Ag-Cu brazing foil of about 0.004” thick in either H_2 furnace or vacuum furnace at about 800°C. The seal is then subjected to helium leak testing, and high pressure (hydraulic upto 250 bar) testing depending on the application of seal. Fig 2. shows photograph of a CM seal for vacuum (a), and schematic and photograph of a CM seal for high pressure application (b & c).
In the case of active brazing alloy technique, the intermediate step of metallizing ceramic tube is avoided. Titanium is one of the important elements, which is used as active component in the brazing material. Controlled addition of Ti to common FCC filler metals like Cu, Au, Ag, Ni and their alloys, have been shown to facilitate wetting of aluminum, zirconium through the formation of TiO, Ti₂O₃ layers. The process involves the entire operation in vacuum or inert atmosphere for reproducible results. Some common active brazing alloy compositions used for sealing are 63Ag-35.25Cu-1.75Ti, 70Cu-21Sn-9Ti, 90Ag-10Ti, 64.8Ag-25.2Cu-10Ti etc. Brazing alloy of composition 70Cu-21Sn-9Ti has been successfully used for bonding with alumina by Shuie et al [24]. After seal fabrication various acceptance tests are carried out.

3.2 Glass-ceramics- to-metal seal
LZS glass-ceramics are reported to be suitable for fabrication of matched type hermetic seals with a variety of metals and alloys. We shall focus on the preparation of matched type hermetic GCM seals with LZS and Cu and SS321 metal/ alloys. Two different lithium zinc silicate glasses of nominal compositions (wt.%) (a) low zinc content (LZSL), Li₂O: 12.65, ZnO: 1.85, SiO₂: 74.4, Al₂O₃: 3.8, K₂O: 2.95, P₂O₅: 3.15, B₂O₃: 1.2, and (b) high zinc content (LZSH), Li₂O: 8.9, ZnO: 24.03, SiO₂: 53.7, Na₂O: 5.42, P₂O₅: 2.95, B₂O₃: 5.0 were prepared by usual melt and quenched technique. The details of the experimental procedure are discussed by Sharma et al. [9]. NiO doped LZSH glass having the nominal composition Li₂O: 15, ZnO: 4.0, SiO₂: 54, NiO:1.0, Na₂O:50, B₂O₃: 19.0, P₂O₅: 2.0, was also prepared for the fabrication of GCM seal. As the thermal expansion coefficient (TEC) of LZS glass-ceramics matches with TEC of Cu and SS 321, LZS glass-ceramics to Cu and SS-321 matched type hermetic seals withstand vacuum of 10⁻⁶ Torr and leak rate of 10⁻⁹ Torr.l/sec, were fabricated with both LZSH and LZSL compositions.
The Cu and SS 321 metal/alloys were used both as metal housing as well as central pins in seal fabrication. The metal housing and the central pins were first cleaned with chemical solution and then heated (950°C) under flowing wet H₂ gas to remove all the oxide impurities from the surface and give coating of thin oxide layer on the surface. The whole assembly consisting of metal housing, pins and glass (either preform/frit) supported by graphite jig is placed inside the furnace for heat treatment in N₂ atmosphere. The seals are prepared using two different heat treatment schedules; i) heating schedule (HS), and ii) cooling schedule (CS) for both the compositions.

In case of heating schedule as shown in Fig.3, the furnace temperature is raised to about 950°C to melt the glass and held there for 45min before cooling down to a temperature about 480°C at the rate of 5°C/min. This held there for 120min and then the temperature is increased to the first crystallization temperature (640°C) followed by second crystallization temperature (750°C). At each temperature, the sample is held for 60min. The temperature is then lowered to 450°C for annealing followed by cooling down to the room temperature. In the case of cooling schedule (CS), first the temperature of the sealing assembly was raised to melting temperature (950°C). After 45min of dwell time at this temperature, it was lowered to higher crystallization temperature (750°C) and then to lower crystallization temperature (640°C) at the rate of 5°C/min. Dwell time at both the temperatures was 60min. After crystallization, the assembly was cooled down to annealing temperature of 450°C and held for 120min for annealing. Finally, the temperature was decreased to room temperature at the rate of 3°C/min. For multipin seals fabrication, LZS composition was modified by adding about 1 wt% of NiO.

![Fig. 3 Schematic of sealing cycle using heating schedule (HS) for LZSL glass-ceramics to Cu/SS 321 seal fabrication.](image)
Photograph of LZS glass-ceramics-to-Cu/SS321 multipin matched type seal is shown in the Fig. 4. These seals are found to withstand a vacuum of $10^{-6}$ Torr with leak rate of $10^{-9}$ Torr.lit/sec. Fig. 5 shows compressive type single pin seal prepared using lithium aluminum silicate glass-ceramics and SS304 housing with SS446 central pin. This seal showed high pressure endurance of 12000psi.

3.3 Interface study on LZS glass-ceramics seal

The interface of LZS glass–ceramic to SS-321 alloy seal was studied for microstructure and various elemental interdiffusion using CAMECA SX 100 EPMA. The joined seal is trimmed, polished and etched with 10% HF. Lithium fluoride (LiF), penta erithrotol (PET) and thallium acid phthalate (TAP) crystals were used for diffracting X-rays. X-rays analysis was done using 20 kV acceleration voltage and 100 nA beam current.

3.3.1 LZSL glass-ceramics to Cu interface

Back scattered electron (BSE) image of LZSL glass-ceramic close the Cu metal interface and SS interface were studied. In case of Cu interface shows two types of microstructure indicating presence of different phases in the glass-ceramics. These phases were identified as cristobalite (SiO$_2$) and Li$_2$SiO$_3$ from X-ray diffraction studies. Wavelength dispersive spectroscopy (WDS) analysis showed that the matrix is homogeneous in nature and essentially consists of Si, with very small amount of Zn and P. Whereas Li could not be detected using EPMA. Electron microprobe line scans showed a gradual change in Cu and Si concentrations, across the interface confirming interdiffusion of Cu and Si.

3.3.2 LZSL glass-ceramics to SS 321 interface

BSE image of interface area of LZSL glass-ceramic sealed with SS-321 metal housing [Fig. 6(a)] shows a similar microstructure as in the case of Cu, but a thick layer rich in Cr is precipitated at interface [Fig. 6 (b)]. This is confirmed from electron microprobe line scans taken for Cr as shown in Fig. 7(a). Fig 7(b, c and d) shows the electron microprobe line scans for Ni, Fe and Si. This shows gradual change in the concentrations of elements across the LZSL glass-ceramic to SS-321 interface.
The electron microprobe line scan of Si shows the presence of some amount of Si along with Cr and possible formation of Cr$_2$Si$_3$ or LiCr(SiO$_3$)$_2$ thick layer at the interface. Si line scan also confirmed diffusion of Si towards the metal region across the Cr-rich layer. Strong adhesion between the glass-ceramic and SS-321 is promoted by the elemental interdiffusion of Fe, Cr, Ni and Si together with the formation of a thick layer rich in Cr at the interface and forming their oxides.

Fig. 6 (a) BSE image for LZSL glass-ceramic with SS-321 interface  (b) X-rays images at the glass-ceramic/metal interface for the element Cr.

Fig. 7 Electron microprobe line scans across the LZSL glass-ceramic to SS-321 interface  (a) Cr element showing diffusion and formation of a layer of Cr across the interface. (b) Fe (c) Ni showing Fe and Ni diffuses from SS 321 to glass-ceramic across interface (d) Si element diffuses from glass-ceramic to metal interface.
On the other hand, the interface in LAS glass-ceramics to SS304 compressive seal did not show any interdiffusion. However, there was a marked difference in the microstructure of LAS in presence and absence of metal housing.

In our effort to develop sealant for high temperature CaO-TiO$_2$-P$_2$O$_5$ (CTP) based glass/glass-ceramics is prepared. A sandwich seal crofer$22$-CTP-Crofer$22$ was fabricated. Fig.8 shows microstructure of interface of CTP-Crofer$22$. This shows a good bonding at the interface due to interdiffusion of Ca and Fe however some voids are observed in the glass-ceramics region possibly formation of calcium phosphate phase. The process need to be optimised along with some additives to prevent such void for producing defect free interface.

Fig. 8 Microstructure of the CTP glass-ceramics –to –Crofer$22$ interface.

4. Conclusions
Ceramics to metal seals withstanding a vacuum of $10^{-6}$ Torr with helium leak rate less than $10^{-9}$ Torr l/s and high pressure up to 250 bar have been fabricated using conventional metallization technique. The composition and process parameters for LZSL and LZSH were optimised to prepare hermetic seals with both Cu and SS 321. In case of LZSL-to- Cu matched seal, interdiffusion of Cu and Si and in case of LZSH glass-ceramic-to-SS matched sea,l inter diffusion of Cr, Fe, Ni and Si at the interface promote strong adhesion between glass–ceramics and metal. On the other hand there was no diffusion across the interface of LAS glass-ceramics to SS 304 compressive seal.

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References
[1] W. D. Kingery, H. K. Bowen and DR Uhlmann, “Introduction to Ceramics” John Wiley & sons, NY, (1976).
[2] W. J. McCraken: “Corrosion of Glass, Ceramics, and Ceramic superconductors” (Eds. D C Clark and B K Zitois. Park Ridge: Noyes, (1992) p. 432.
[3] O.V. Paiva and M.A. Barbosa, in “Advances in Materials Science and Implant Orthopaedic Surgery”, edited by R.Kossowsky and N.Kossowsky (NATO ASI Series, Dordercht, Netherlands (1995) p.275.
[4] H. Hongqi, J.Zahao and W. Xiaotian, J. Mater. Sci. 29 (1994) 5041.
[5] M. L. Santella. Ceram. Bull. 6 (1992) 947
[6] M. M. Schwartz. “Ceramic Joining” (ASM International, Ohio, USA, 1990)
[7] I.W. Donald, B.L. Metcalfe, D.J. Wood, J.R. Copley, J. Mater. Sci. 24 (1989) 3892-3903.
[8] B.L. Metcalfe and I.W. Donald, Conf. Series on the International Conf. on New Materials and their Applications, IOP, Bristol, 111 (1990) 469.
[9] B.I. Sharma, Madhumita Goswami, P. Sengupta, V.K. Shrikhande, G.B. Kale and G.P. Kothiyal, Materials Letters 58 (2004) 2423.
[10] I.W. Donald, J. Mater. Sci. 28 (1993) 2841.
[11] A. Zanchetta, P. Lefort, J. Eur. Ceram. Soc. 15 (1995) 233.
[12] A. Zanchetta, P. Lortholary, P. Lefort, J. Alloys Compd. 22 (1995) 86.
[13] T.R. Anthony, J. Appl. Phys. 54 (1983) 2419.
[14] Shobha Manikandan, Jagannath, V K Shrikhande and G P Kothiyal, Anti-Corrosion Method and Materials 53 (5) (2006) 303.
[15] V. K. Shrikhande, V. Sudersan, G. P. Kothiyal, and S K Kulshreshtha, J. Non-Cryst. Solids 283 (2001) 18.
[16] K. V. Shah, M. Goswami, M. N. Deo, A. Sarkar, S. Manikandan, V. K. Shrikhande and G. P. Kothiyal, Bulletin of Materials Science, Science 29(1) (2006) 43.
[17] Madhumita Goswami, P. Sengupta, Kuldeep Sharma, Rakesh Kumar, V. K. Shrikhande, J. M. Ferreira and G P Kothiyal, Ceramics International, 33(5) (2007) 863.
[18] B.W. King, H.P. Tripp, W.H. Duckworth, J. Am. Ceram. Soc. 42 (11) (1959) 504.
[19] A. P.R. Sharps, A.P. Tomsia, J.A. Pask, Acta Metall. 29 (1981) 855–865.
[20] R.B. Adams, J.A. Pask, J. Am. Ceram. Soc. 44 (1961) 430–433.
[21] A.G. Eubanks, D.G. Moore, J. Am. Ceram. Soc. 38 (1955) 226–230.
[22] W.F. Yext, B.J. Shook, W.S. Katzenberger, R.C. Michalek, IEEE Transactions on Components, Hybrids, and Manufacturing Technology, CHMT 6 (4) (1983) 455.