Development issues in glass-ceramic seal materials for planar SOFC stacks

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Types of seals for p-SOFC

Rigid seals

- Glass and glass–ceramic sealants, Brazes

Compressive seals

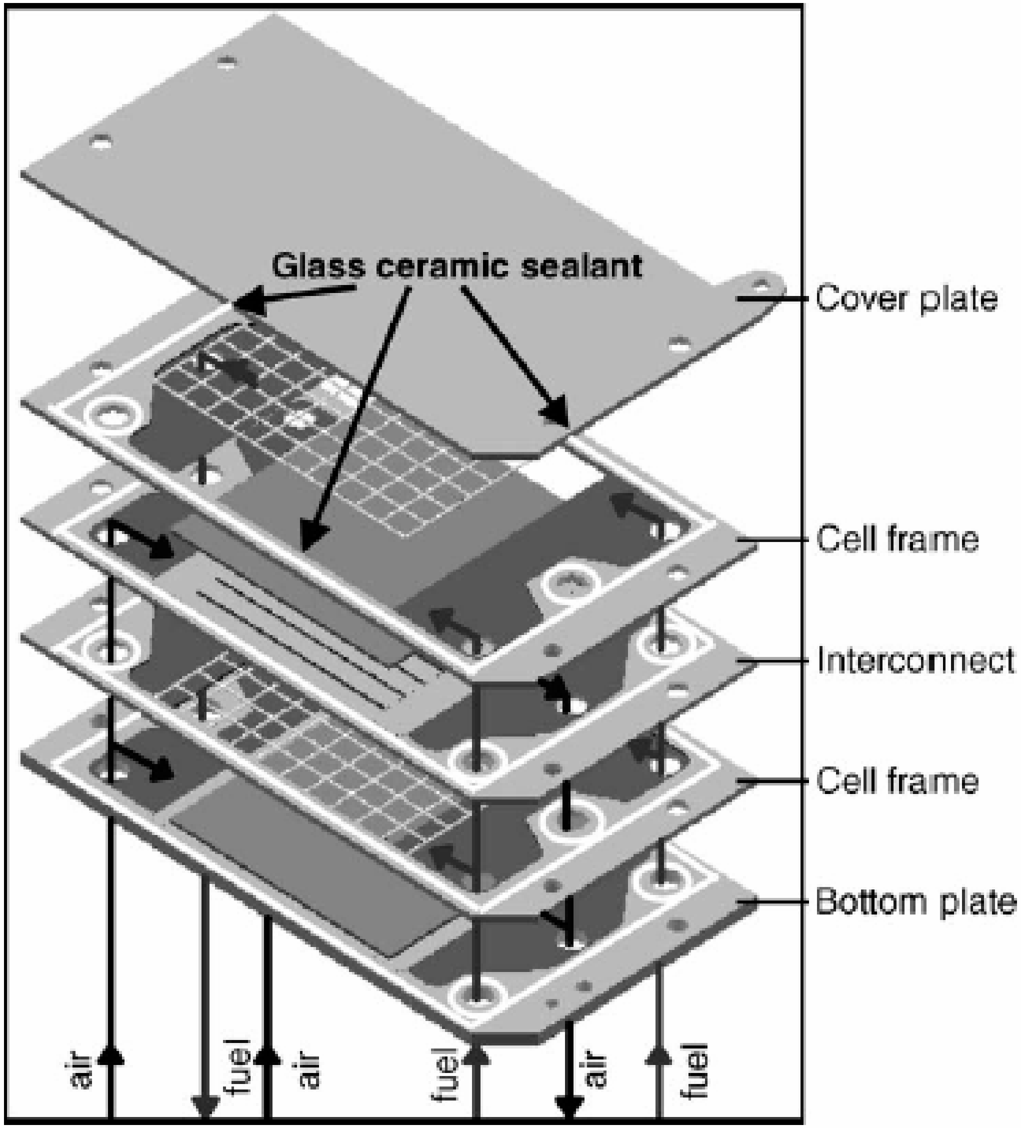
- Metallic compressive seals, Mica-based compressive seals

Rigid with embedded phase

•structurally yieldable at high operating temperatures to absorb stresses

-increased seal durability & stress absorption

Typical requirements



Glass-ceramic seals for SOFC

Typical requirements

- Electrical insulation: $\rho \geq 10^4\ \Omega$ cm
- Tailored CTE: 9–12 X 10^{-6} K^{-1}
- Viscosity

  @sealing temp. : 10^6–10^9 dPa s

  @working temp. : ≥ 10^9 dPa s
- Good adherence to :Zirconia, NiYSZ, SS

- **flow ability of glass for wetting and sealing**
- **hermetic sealing**
- **preventing diffusion of ions**
- **no devitrification over a long period of time**
- **Tailoring of the bulk properties**
- Diffusing the stress arising from thermal and redox expansions and contractions produced by the system

The Glass-Ceramics Process

- **Melting and Fritting :** homogeneous dispersion, forming shapes
- **Heat-treatment :** converting to microcrystalline ceramics, enhancing much superior properties than the starting glass

  - **Sealing** — *10^6–10^9 poises** — for IT-SOFC application typically ~850^{o}C of a glass softening at ~770^{o}C
  - **Nucleation** — *10^{11}-10^{12} poises** — invisible growth centers by nucleating agent; large nos of tiny embryos N=10^{13} to 10^{20} m^{-3}
  - **Crystallisation** — exothermic effect – DTA, XRD

**viscosity at annealing point is 10^{13} poises*

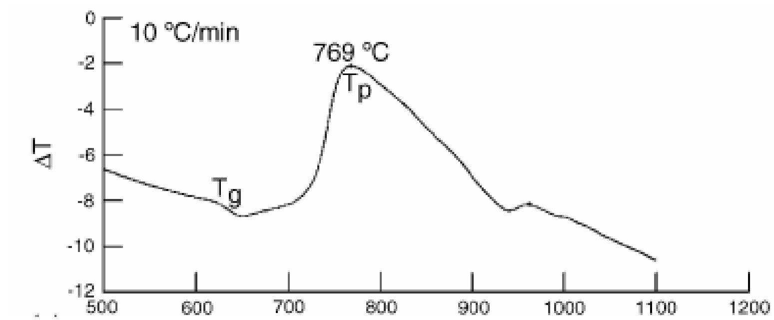
rate

Glass-ceramic seals for SOFC

Example: **BCBAS** seal composition for SOFC

$$35\mathbf{Ba}O–15\mathbf{Ca}O–5\mathbf{Al}_2O_3–10\mathbf{B}_2O_3–35\mathbf{Si}O_2 \text{ (mol\%)}$$

CRYSTALISATION



Crystalline phase development in BCAS glass on heat treatments

Heat treatment		Crystalline phases detected from X-ray diffraction					
Temperature (°C)	Time (h)	Amorphous	$BaSiO_3$	Hexacelsian	Celsian	$(Ba_{1.5}Ca_{0.5})SiO_4$	$(Ba_{1.31}Ca_{0.69})SiO_4$
700	20	X					
	50	X	X				
750	3	X					
	5	X	X				
	10	X	X				
	100	X	X	X	X		
800	1	X	X				
	5	X	X	X			
	18	X	X	X		X	
	50	X	X	X		X	
	100	X	X	X			
850	21	X	X	X			
	100	X	X		X		X
900	10	X	X	X			
	100	X	X	X			
1000	10	X					
	50	X					

CTE of crystalline phases

Coefficients of thermal expansion of crystalline phases formed in alkaline-earth glass–ceramics

System	Phase	CTE (°C^{-1} × 10^{6})
Mg–Si–O	Enstatite ($MgSiO_3$)	7–9
Ca–Si–O	Wollastonite ($CaSiO_3$)	4–9
	Calcium orthosilicate (Ca_2SiO_4)	10–14
Ba–Si–O	Barium silicate ($BaSiO_3$)	9–13
	Barium orthosilicate ($BaSi_2O_5$)	14
Ba–Ca–Si–O	Barium calcium orthosilicate ($Ba_3CaSi_2O_8$)	12–14
Mg–Al–Si–O	Cordierite ($Mg_2Al_4Si_5O_{18}$)	1
Sr–Al–Si–O	Hexacelsian ($SrAl_2Si_2O_8$)	8–11
	Monocelsian ($SrAl_2Si_2O_8$)	3
	Orthocelsian ($SrAl_2Si_2O_8$)	5–8
Ba–Al–Si–O	Hexacelsian ($BaAl_2Si_2O_8$)	7–8
	Monocelsian ($BaAl_2Si_2O_8$)	2–3
	Orthocelsian ($BaAl_2Si_2O_8$)	5–7

Glass-ceramic families in the SOFC sealing party

System	Typical Composition (mole %)					
	SiO_2	**B_2O_3**	**Al_2O_3**	**BaO/SrO**	CaO/MgO	Other
Silicate	35	-	-	44 Bao	11 Cao	10
Aluminosilicate	50	-	5	45 BaO	-	
Borate	8	40	7	25 SrO	-	20 La_2O_3
Borosilicate	33	3	-	40 BaO	10 CaO	14
Boroaluminosilicate	33	17	10	35 BaO	-	5 La_2O_3
Boroaluminosilicate (with alkali)	26.8	40.5	4	-	22.7 CaO	6 K_2O

Glass-ceramic systems for SOFC sealing applications

General formulation from the current patent disclosure:

Component (mol%)	Range	preferably
Glass-former ($SiO_2+B_2O_3$)	50-75	60-70
Total Alkalies(K_2O+Li_2O)	less than 10	
Alumina (Al_2O_3)	low	2-5
ZrO_2, ZnO, TiO_2	less than 5	less than 5
High CTE fillers (YSZ, Ca-SZ, etc)	10-20	

The role of Alumina in glass-ceramic compositions

	SiO_2	B_2O_3	Al_2O_3	BaO/SrO Li_2O	CaO/MgO	Other
Borate	8	40	7	25 SrO	-	20 La_2O_3
Borosilicate	33	3	-	40 BaO	10 CaO	14
Boroaluminosilicate	33	17	10	35 BaO	-	5 La_2O_3
CTI-1	**74.4**	**-**	**-**	**23 Li_2O**	**1.7 K_2O**	**0.8 P_2O_5**
CTI-2	**74.2**	**-**	**0.3**	**23 Li_2O**	**1.7 K_2O**	**0.8 P_2O_5**
CTI-3	**73.6**	**-**	**1.1**	**23 Li_2O**	**1.7 K_2O**	**0.8 P_2O_5**
CTI-4	**71.9**	**-**	**2.1**	**23 Li_2O**		**0.8 P_2O_5** **1.7 K_2O**
Boroaluminosilicate (with alkali)	26.8	40.5	4	-	22.7 CaO	6 K_2O

Study of complex rheological behavior of the micro-heterogeneous matrix during heating process

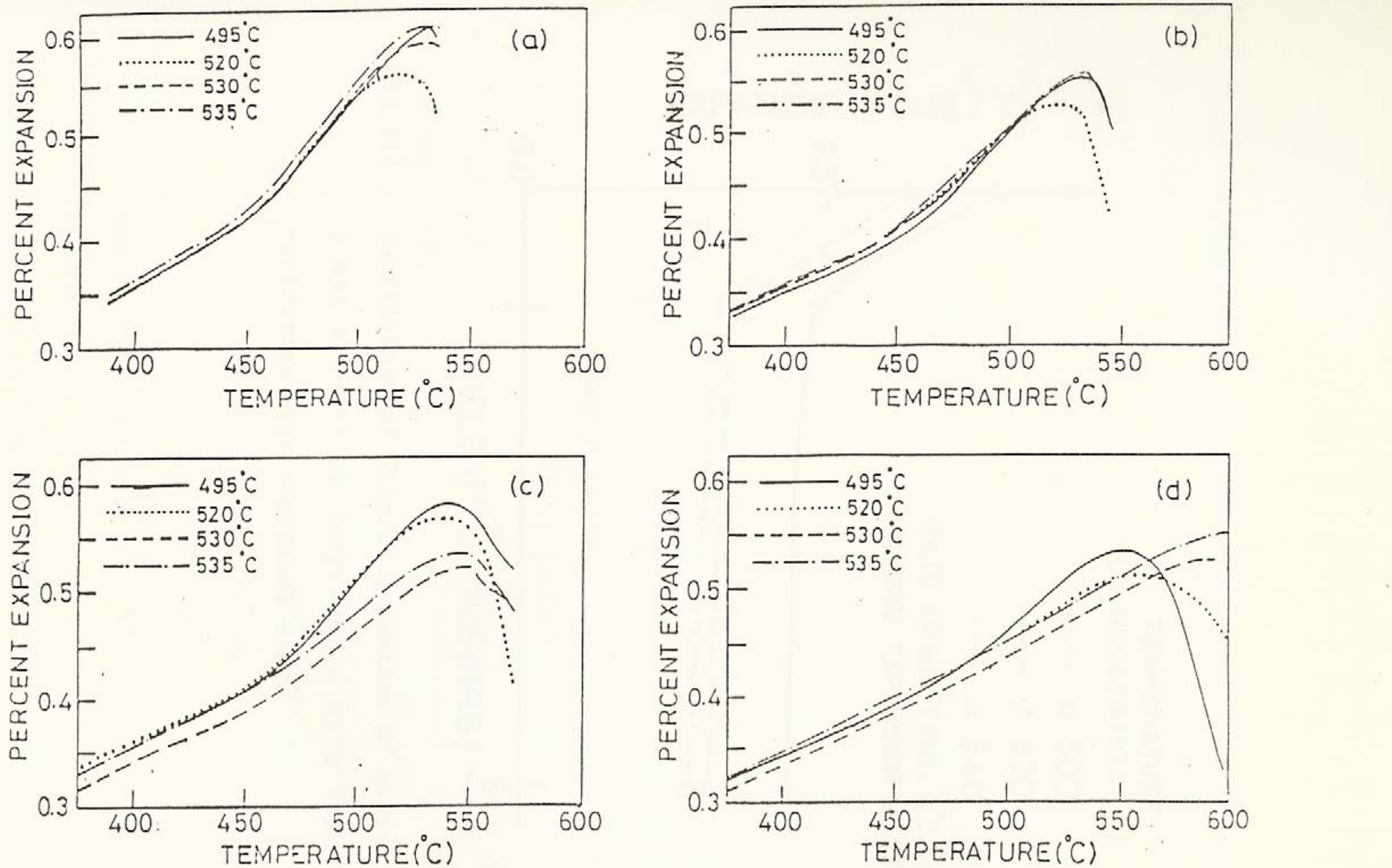


Fig.III.2. Linear thermal expansion behavior of Glass-II nucleated at indicated temperatures for (a) 10 min, (b) 20 min, (c) 40 min and (d) 60 min. Rate of heating during the expansion measurement: 10°C/min.

Study of complex rheological behavior of the micro-heterogeneous matrix during heating process

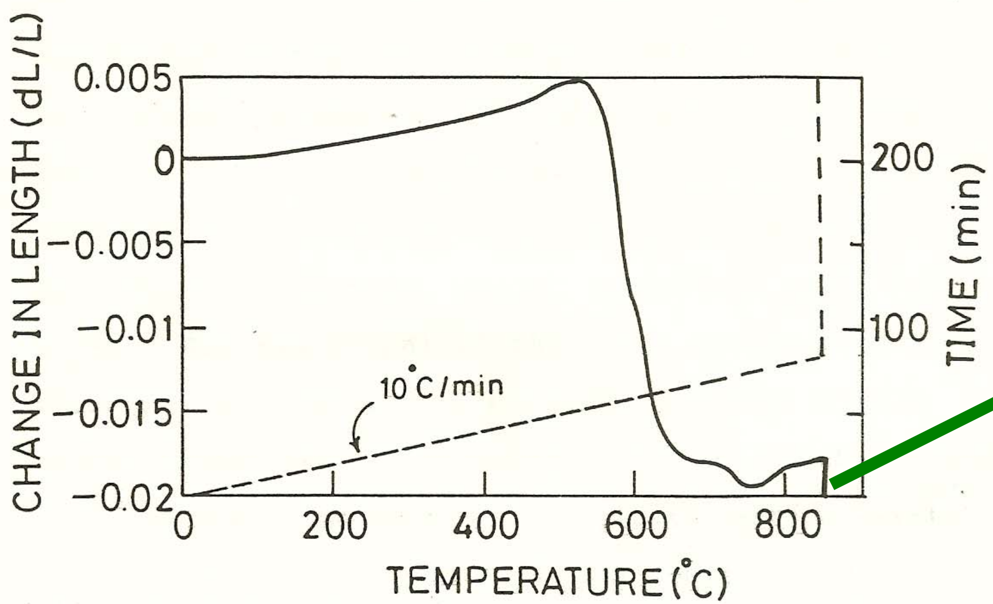
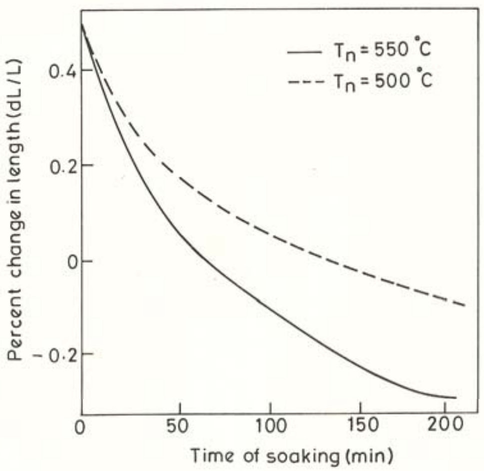
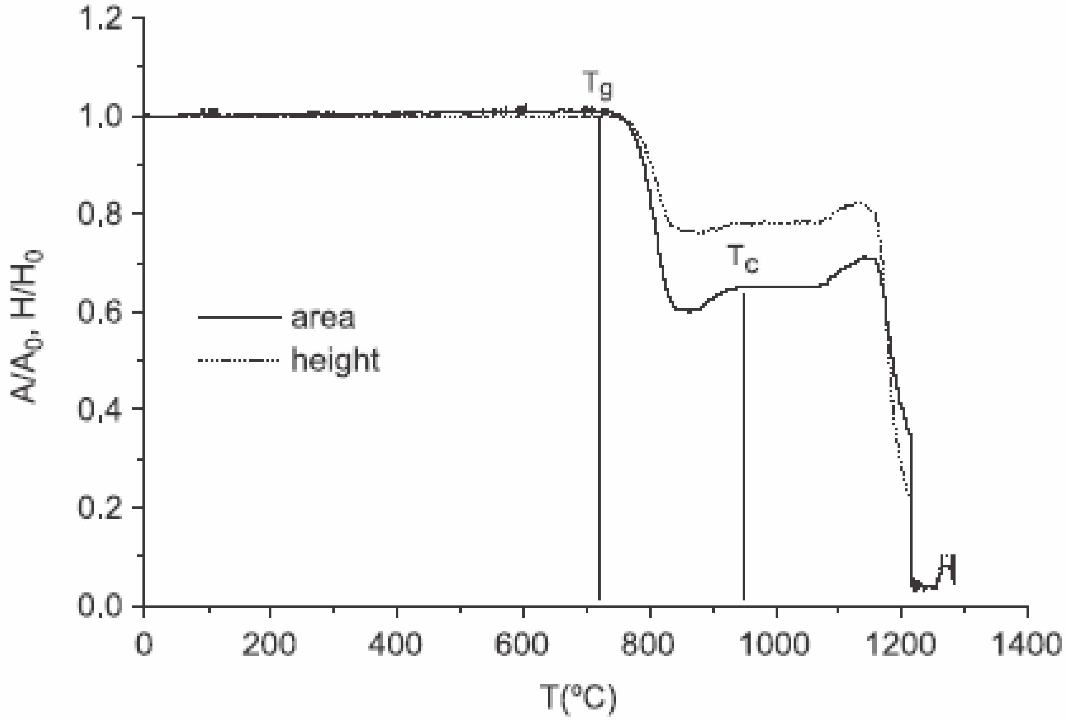
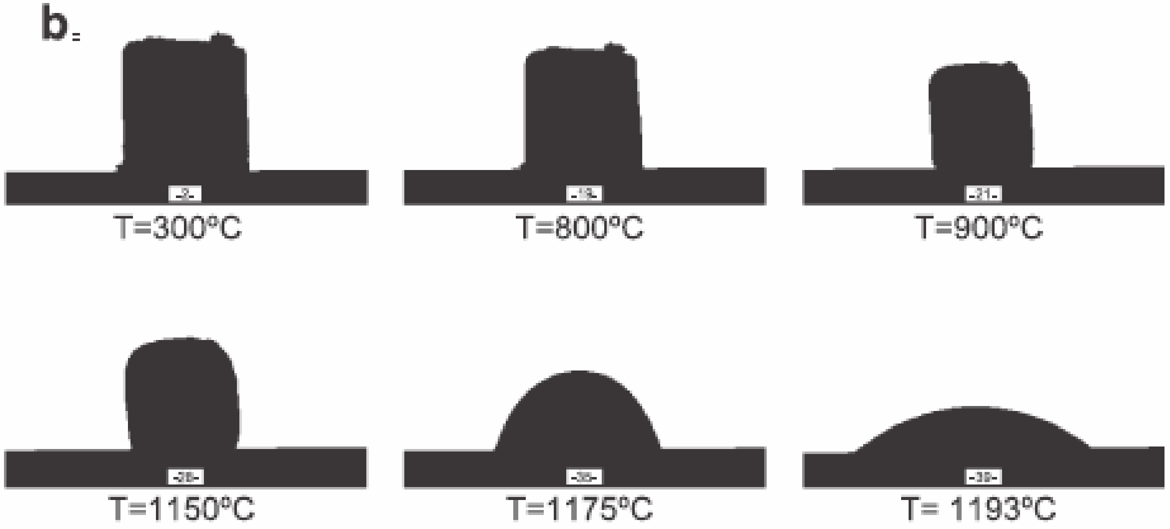


Fig.III.5. Change in length (dL/L) of the nucleated (95 min at 500°C) glass II rod as a function of temperature of heating at the rate of 10°C/min in a horizontal push rod dilatometer furnace and 200 min soaking after reaching 847°C.



Variation of area & height of the samples with increasing temperatures at hot stage microscope





the sintering of glass powders should be completed before crystallization

Study of optimum nucleation process by indirect methods

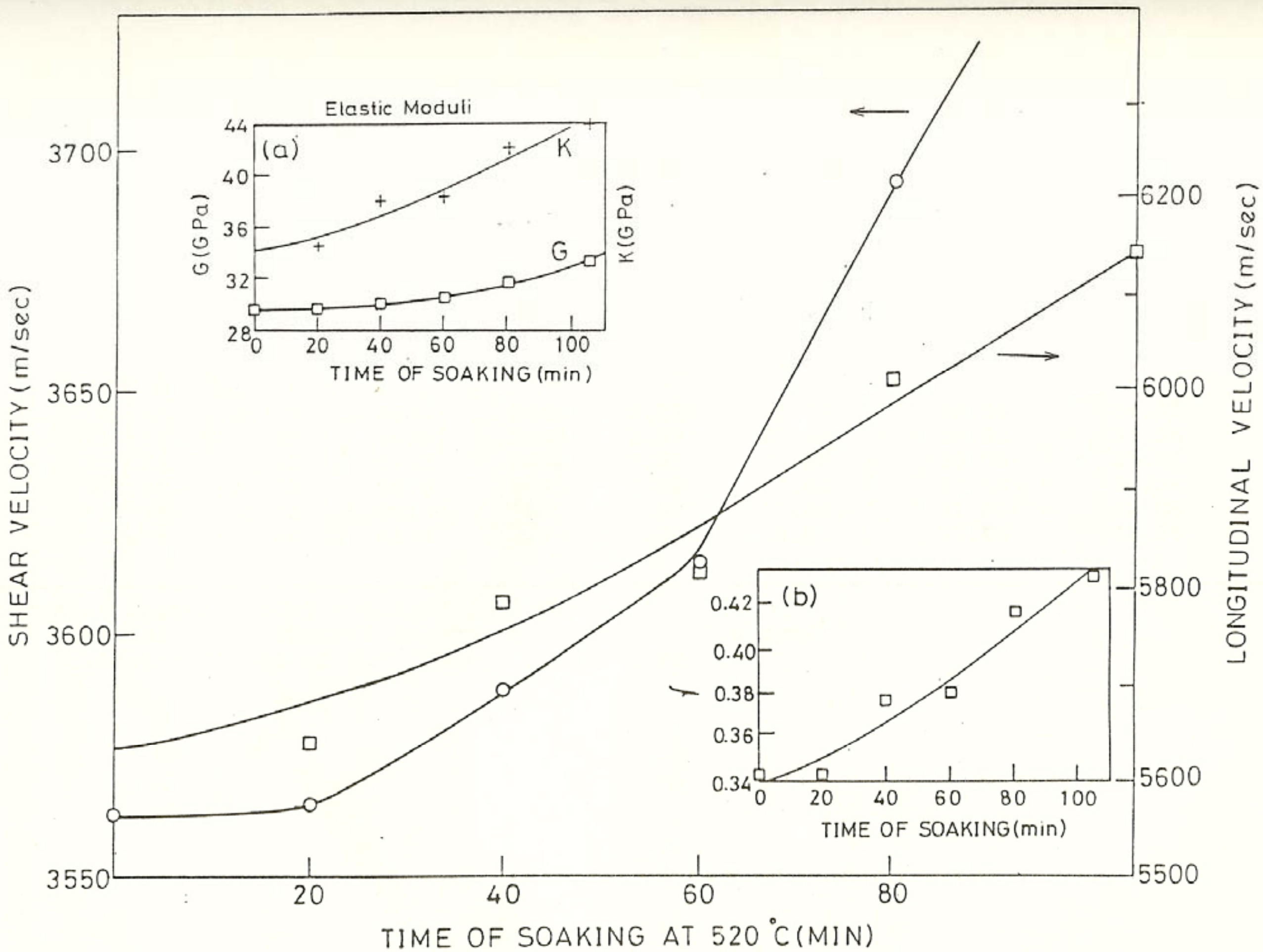
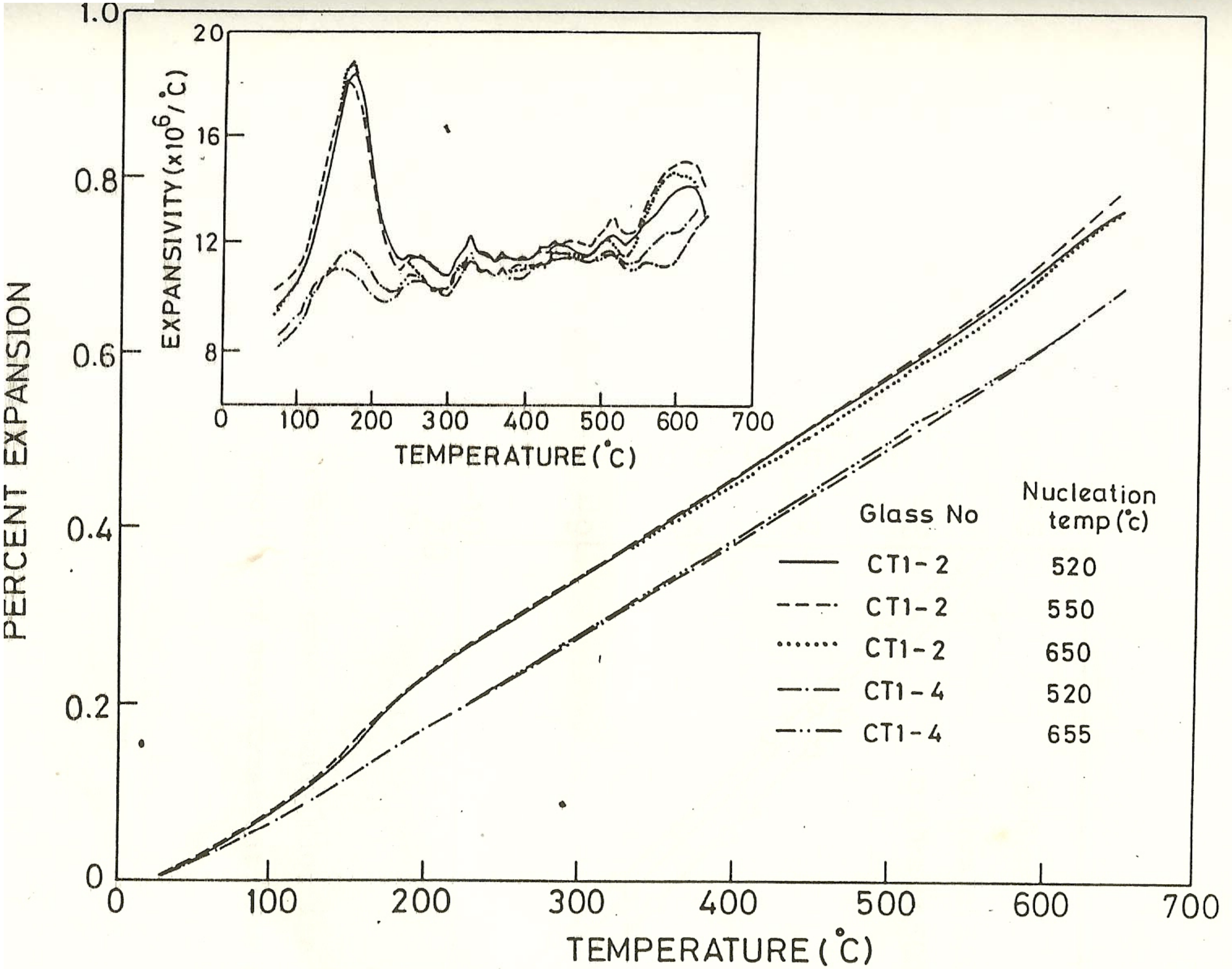
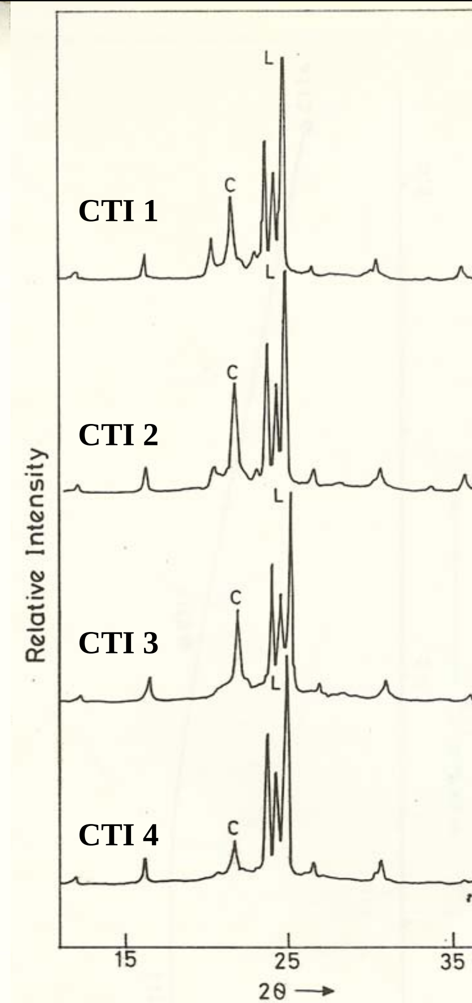


Fig.III.9. Ultrasound velocities (both longitudinal and shear) in glass-I as a function of nucleation soak time. Variations of bulk and shear moduli are shown in inset (a). In inset (b) variation of Gruneisen parameter is shown.

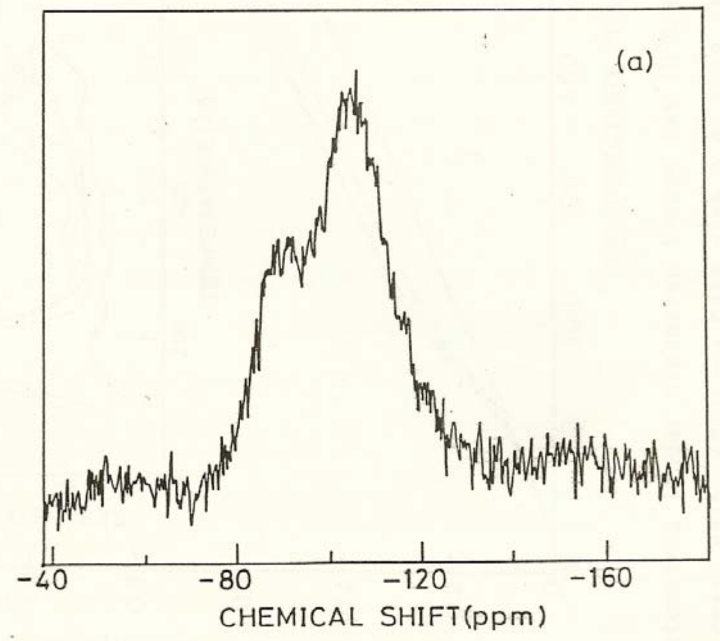
Glass-ceramic seals for SOFC



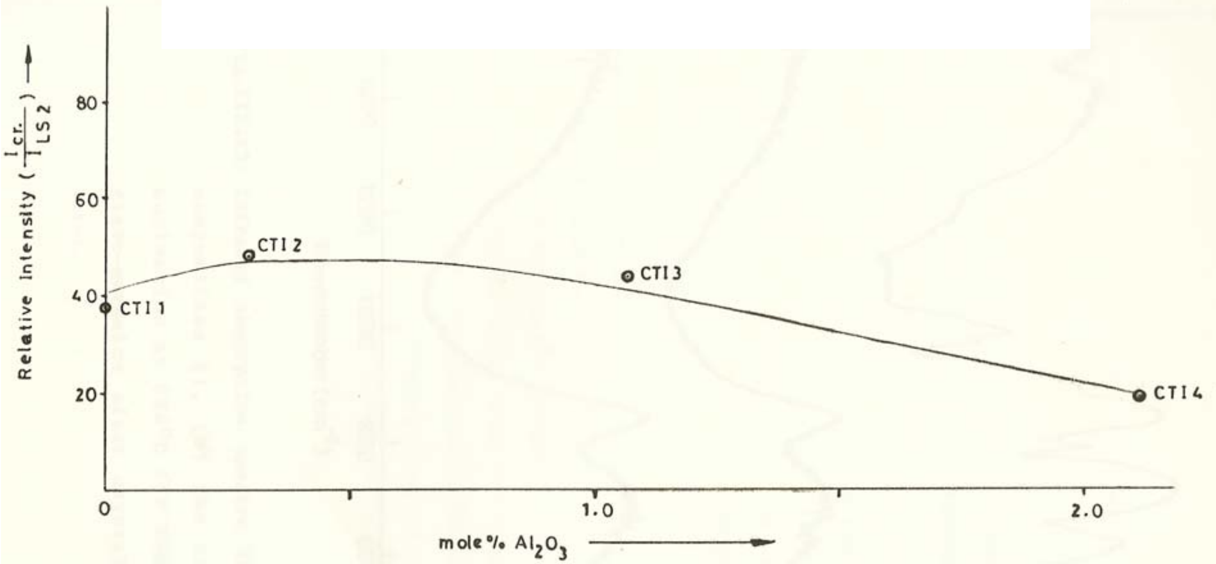


. Dilatometric linear expansion traces (at 10^{o}C/min heating rate) of glass nos. CTI2 and CTI4 crystallized together but nucleated at different temperatures as indicated. Expansivities (coefficients of thermal expansion) for the same materials are plotted in the inset after smoothening the graph by taking running average of the expansivities at every 10^{o}C intervals.

^{27}Al MASNMR spectra of the Glass-ceramics CTI-4 (with 2 mol% Alumina).



A plot of relative intensities of crystobalite and lithium disilicate peaks as a function of mol% Alumina).

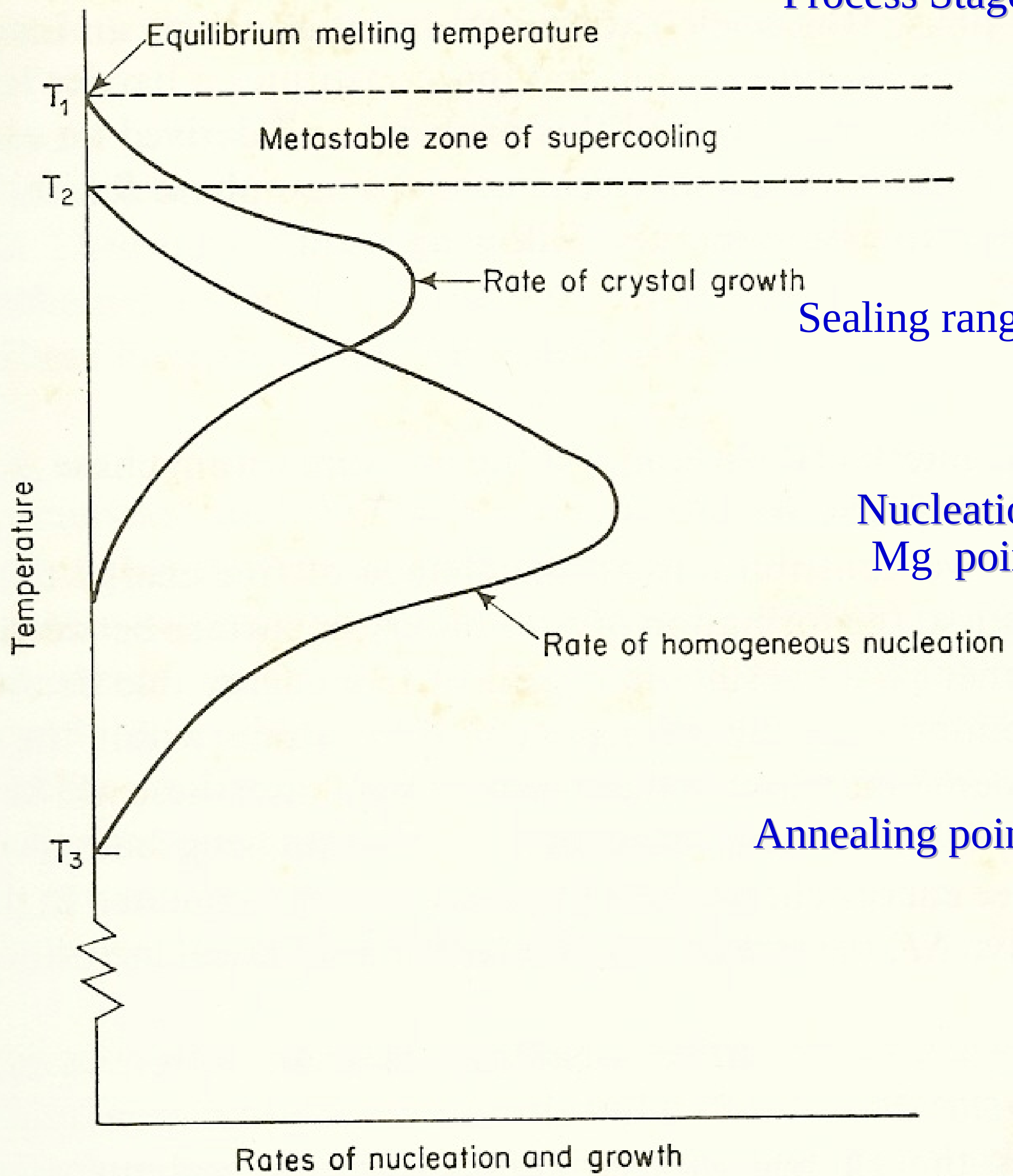


Conclusion

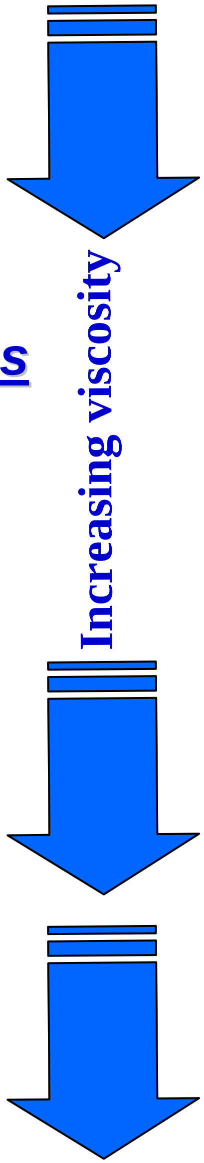
Major glass-ceramic systems used in SOFC sealing applications are discussed with considerations involved for selecting batch components and their proportions. Based on the knowledge of the glass-ceramic principles, the processing conditions may be designed for adequate wetting and sealing before strengthening the glass by crystallization.

Thank You

Glass-ceramic seals for SOFC



Process Stages	Viscosity values
	10^2 poises
Sealing range	10^6–10^9 poises
Nucleation Mg point	10^{11}-10^{12} poises
Annealing point	10^{13} poises



back

Silver is an especially useful component in the low-melting-point seal described herein. Silver does not typically form a high temperature oxide and is therefore stable in an oxidizing environment, such as within a fuel cell stack. Pure silver is soft and yieldable, and has an appropriate melting temperature, but has a rather high thermal expansion coefficient and does not adhere particularly well to ceramics. This lack of adherence can be addressed by using a wettable layer (350), as described above, or by mixing the silver with an additive.

0044] One class of additives that can be used with silver in a low-melting-point seal are glasses, for example, boro-alumina silicate glass, boro-baria silicate glass, etc. The glass and silver are mixed to form a composite material. The result is a glass-silver composite because the two components stay segregated.

[0045] Glass-silver composite seals appear to have excellent wetting and adhesion on both stainless steel and ceramics and result in an excellent seal. Glasses can be chosen for the composite such that the combined thermal expansion coefficient matches the housing (100), manifold and/or fuel cell (320).

In FIG. 3B, a seal (360') is made from a glass-silver composite material in which there is a glass matrix (370) and silver (380) as a discontinuous embedded phase. Such a seal (360') has many advantages including better heat transfer, greater compliance, and a greater range of glass chemistry through thermal expansion coefficient matching with the help of the high-expansion silver. Other conductive metals, as mentioned herein, may also be used in the seal of FIG. 3B as the embedded phase, in place of silver.

[0048] Additionally, as mentioned above, the low-melting-point seal (360') may also include any number of particles, fibers, rods, spheres or other forms of "filler material." This "filler material" may be incorporated in the low-melting-point seal (360') in order to more closely match the thermal coefficient of expansion (TCE) of the seal with the TCE of the fuel cell housing (100) or other materials that may be surrounding the fuel cell. Moreover, the "filler material" may also provide additional surface tension to keep the seal (360') in place when the SOFC operates above the melting point temperature of the low-melting-point seal (360). The "filler material" may be any number of conductive or insulating materials including, but in no way limited to, tungsten (W), molybdenum (Mo), zirconium di-oxide (ZrO.sub.2), magnesium oxide (MgO) or cerium oxide (CeO.sub.2).

While the construction of the SOFC housings (100; FIG. 3) using stainless steels and other less expensive materials is advantageous in reducing the overall cost of SOFC stacks, these materials suffer from differing thermal conductivities and thermal coefficients of expansion (TCE). As a result, non-uniform thermal expansions often occur when the housings are placed in stack configurations. Non-uniform thermal expansion of the SOFC housings may produce thermal stresses. These thermal stresses have traditionally been transferred from the housings, through rigid seals, and onto the SOFCs. The transfer of thermal stresses reduces the operating life of the SOFC systems by either causing failure in the SOFC, failure in the rigid seals, or both. However, when thermal stresses caused by the expansion and contraction of the metalized areas are transferred to the present low-melting-point seal, the liquid or softened alloy of the low-melting-point seal yields in response to the thermal stresses (step 640). By yielding in response to thermal stresses, the present low-melting-point seal prevents the transfer of the thermal stresses from the SOFC housing to the somewhat brittle SOFC. This yielding in response to thermal stresses continues until the reaction cycle ceases and the operating temperature of the SOFC housing is reduced to its original temperature (step 650). As the temperature is decreased, the low-melting-point composite material re-solidifies into its original position and structure.

Glass-ceramic seals for SOFC

Even if the coefficients of thermal expansion are matched, the rates of thermal conductivities within a stack are typically not matched, resulting in non-uniform thermal expansion. As glass is inherently brittle, it cracks and fails under thermal cycling conditions. The brittleness of glass also makes glass seals subject to failure as a result of jarring shocks or vibrations.

The fibres may be randomly oriented. In a preferred embodiment, the seal may be precompressed prior to use.

[0009] The ceramic fibres may be selected from the group comprising alumina, zirconia, titania, magnesia or silica. The solid particles may be ceramic particles, glass particles or other inert materials able to resist degradation and sintering at the operating temperatures of the SOFC stack. If the particles are ceramic particles, the particles may be selected from the group comprising alumina, zirconia, titania, magnesia or silica.

[0010] In one embodiment, a substantial portion or all of the particles are submicronic ceramic particles. Preferably, the particles have a particle size of about 0.50 .mu.m or less. More preferably, the ceramic particles comprise a first portion and a second portion wherein the particle size of the first portion is larger than the particle size of the second portion. The first portion may have a particle size of about 0.50 .mu.m and the second portion may have a particle size of about 0.17 .mu.m or less. In another embodiment, the first portion may have a particle size of about 0.50 .mu.m and the second portion may have a particle size of less than about 0.06 .mu.m. The proportion of larger particles to smaller particles may be varied to achieve maximum sealing performance.

Glass-ceramic seals for SOFC

One of the major challenges for implementation of solid oxide fuel cells (SOFCs) is the development of suitable sealant materials to separate the air and fuel. The majority of the planner SOFC stacks require **hermetic sealing** under stringent environmental conditions to prevent gas leakage or cross-leakage. Some specific glass-ceramics seals appear promising after reportedly withstanding in excess of 1000 hours run without degradation in SOFC stack demonstrations. Apart from the constituents of the residual glass-matrix, the nature and amount of crystalline phases to be nucleated and grown in the glass-ceramic seals have the most significant bearing on the key characteristics of the seal namely thermal expansion match, **preventing diffusion of ions**, softening temperature and the **flow ability of glass for wetting and sealing** the cell parts. **Tailoring** of the bulk properties of the seal is achieved by some established tools prescribed in the science and technology of glass-ceramics. These principles with practical examples will be discussed in this talk in relation to the issues connected to SOFC sealing;

- glass-ceramic system design for electrically insulating seals having chemical and mechanical compatibility with cell components under oxidizing and reducing conditions
- choices of crystalline phases for tuning of bulk coefficient of thermal expansion (CTE) and the expansion profile
- influence of stabilization of phases, solid solution, phase separation, nucleation, crystallization kinetics, additives and specific ratios
- key processing considerations while selecting melting or glass powder sintering route, softening points, designing adequate gaps between wetting, nucleation and crystallization temperatures.

Glass-ceramic seals for SOFC

Two major approaches are typically utilized in solid oxide fuel cell sealing practice, namely glass ceramic-based chemical seals and gasket-based mechanical compressive seals. The mechanical compressive seals require a high degree of surface preparation and finish and high-pressure load capacity. A complete hermetic seal oftentimes cannot be achieved due to the flatness limitation of high temperature sintered ceramic cell. Also, contact stresses can readily cause cell fracture during assembly and thermal cycling in SOFC stack operation. Representative examples of mechanical type seals are described and illustrated in U.S. publication No. 2002/0195778, 2003/0203267 and 2003/0215689. Additional examples are set forth in WO 2003/036745 A2, WO 2003/032420 A2 and WO/0217416 A2.

Glass- and glass ceramic-based seals have very good wetting and bonding properties to both ceramic and metals and are capable of forming hermetic seals. Representative examples of this type of sealing for solid oxide fuel cells include U.S. Pat. Nos. 6,291,092, 6,271,158, 6,541,146 and 6,656,625. Additionally EP Publication No. 1211230 A1 discloses a glass matrix composition.