

Gas Permeation Measurements on Low Temperature Cofired Ceramics

R.S. Goeke, R.K. Grubbs, D. Yazzie, A.L. Casias and K.A. Peterson
 Materials Science and Engineering Center, Sandia National Laboratories, Albuquerque, NM
 87185-0959, USA

Abstract

Commercial low temperature cofired ceramic (LTCC) technology is established in microelectronics and microsystems packaging, multichip and radio frequency (RF) modules, and sensors. The ability to combine structural considerations with embedded traces and components using laminated glass-ceramic tapes has created solutions to unconventional packaging requirements of micro-electro-mechanical systems (MEMS) devices. Many MEMS devices such as resonators are very sensitive to pressure and require packaging in a vacuum environment. Attaining and maintaining desirable pressure levels in sealed vacuum packages requires knowledge of the permeation characteristics of the vacuum envelope and the sealing materials.

An experimental system to measure the time dependent gas permeation through LTCC at temperatures from room temperature to 500°C has been developed. This system utilizes a membrane technique in which a gas is allowed to permeate through a test sample, held at a constant temperature, into a high vacuum chamber where it is detected using mass spectrometry. The gas permeation value is determined from the steady state gas flux through the sample. The gas diffusivity and solubility in the material were calculated using data from the time dependent approach to the steady state condition. The gas-solid permeation data for helium through DuPont 951 LTCC is presented and compared to the permeation through other common vacuum envelope materials such as glasses and high-purity alumina ceramics. Application of the permeation data to the prediction of vacuum levels inside typical LTCC packaging is discussed. This data can further be utilized in designs to create LTCC packages that meet specific pressure/time operating requirements.

Key words: Permeation, LTCC, Helium, Diffusion

Introduction

Gas permeability exists, at some level, for almost all materials used in vacuum technology and packaging. This is particularly true of light gases such as helium and hydrogen. Therefore, to achieve and maintain a desired pressure level inside small vacuum packages, a thorough understanding of the permeation characteristics of the package materials is

required. Permeation data exists for many glasses and high alumina concentrations ceramics [1, 2]. Recent interest in fabricating vacuum packages using low temperature cofired ceramics (LTCC) has generated the need for gas permeation data on these packaging materials.

Gas diffusion in solids can be described by Fick's laws. Using a concentration independent diffusion coefficient D , the concentration c of the diffusing species is given by Fick's second law [3]:

$$\frac{dc}{dt} = D\nabla^2 c \quad (1)$$

For diffusion in a planar membrane equation (1) becomes:

$$\frac{dc(x, t)}{dt} = D \frac{d^2 c(x, t)}{dx^2} \quad (2)$$

Permeation of a gas through a membrane involves the following steps:

- (a) Adsorption of the gas to the membrane surface
- (b) Solution/dissociation of the gas from the surface into the bulk
- (c) Diffusion through the membrane
- (d) Dissolution/recombination from the solution to the surface on the low pressure side
- (e) Desorption of the gas from the surface

A diatomic gas, such as hydrogen, would involve the additional steps of dissociation and recombination at (b) and (d). While any of these steps can be rate limiting, permeation which is diffusion controlled, is typically the slow step for reasonably thick membranes [4].

To solve equation (2), we apply the initial and boundary conditions at which the membrane is initially degassed, which is $c(x, t=0)=0$. The concentration on the upstream surface is constant for $t \geq 0$, which is $c(x=0, t)=SP_o^n$ where S is the solubility constant, P_o^n is the upstream pressure and $n = \frac{1}{2}$ for diatomic gases and $n = 1$ for non-dissociative gases. The downstream pressure, which for our experiments is always in high vacuum, is essential zero, $c(x=d, t)=0$. These conditions yield the solution shown in equation (3) when converted to gas flux Q , through a membrane of thickness d [3, 5].

$$Q(x = d, t) = \frac{DSP_o^n}{d} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{Dn^2\pi^2t}{d^2}\right) \right] \quad (3)$$

$$Q(x = d, t = \infty) = \frac{DSP_o^n}{d} \quad (4)$$

$$K = DS \quad (5)$$

$$Q = KP/d \quad (6)$$

Permeability K is proportional to the gas diffusion constant and the solubility constant, equation (5), which can be determined from the equilibrium flow rate. This occurs at long times and is represented by equation (4). K is commonly expressed as the amount of gas ($\text{cm}^3 \text{ STP}$) permeating through a 1 cm^2 area, a thickness of 1 cm and a pressure delta of 1 atmosphere for 1 second . This gives units for K of $\text{cm}^3 \text{ (STP) cm / s cm}^2 \text{ atm}$. The flux or flow rate per unit area of a gas through the membrane material would then be equal to the permeability times the pressure differential over the material thickness or equation (6).

Experimental

The LTCC permeation membranes used in this study were prepared from 0.254 mm thick DuPont 951PX green tape, lot number UF74-1001. The expected shrinkage in the z -direction was 17.86% . Samples of different thickness values were desired and fabricated by layering green tape as shown in Table 1.

Table 1 - LTCC Thickness Fabrication

Number of Layers	Stacking Orientation	Green Thickness (mm)	Fired Thickness (mm)
3	$\uparrow\leftrightarrow\uparrow$	0.762	0.627
4	$\uparrow\leftrightarrow\uparrow\leftrightarrow$	1.016	0.841
5	$\leftrightarrow\uparrow\leftrightarrow\uparrow\leftrightarrow$	1.270	1.052
6	$\uparrow\leftrightarrow\uparrow\leftrightarrow\uparrow\leftrightarrow$	1.524	1.255

The green tape stack was laminated at 70°C and 10.6 MPa for 15 minutes. The laminated stack was then fired in a muffle furnace at 450°C for 120 minutes followed by a hold at 850°C for 45 minutes. Disks with a diameter of 47.63 mm were laser cut from these fired substrates to generate specimens for the permeation test system.

Prior to use, the membranes were vapor degreased with Lenium ES and solvent rinsed with

acetone and isopropyl alcohol. Then the membranes were baked at 760°C in air for one hour.

To improve the vacuum seal in the system and provide a repeatable test area, the perimeter of the disks were coated by sputtering a thin film of 0.2 μm of Cr and 10.0 μm of Ag. The center area was masked with a 3.81 cm diameter disk, yielding a test area of 11.4 cm^2 defined by the thin film metal.

The gas permeation test system was custom designed and built to allow a wide range of temperatures to be cycled while maintaining an excellent vacuum seal. All possible paths for the test gas to reach the mass spectrometer, other than through the test specimen, were eliminated. The specimen mount and heater are placed inside of an independent 1 Pa vacuum jacket as shown in figure 1. The mass spectrometer used was an Ametek quadrupole residual gas analyzer (RGA). The high vacuum side of the membrane is maintained at 10^{-6} Pa by a turbo-molecular pump.

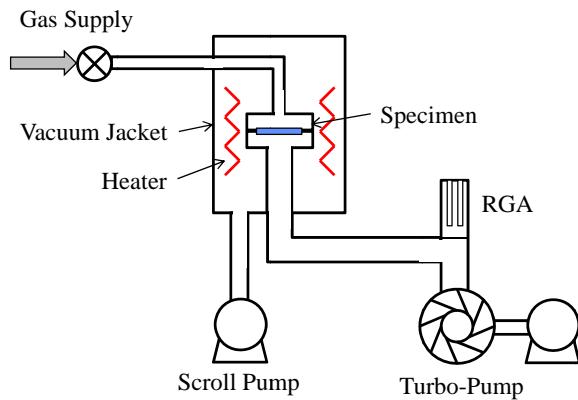


Figure 1 – A schematic of the gas permeation measurement system.

The specimen is sealed on the system using a DN35 stainless steel conflat style flange with two special copper gaskets. The copper gaskets were machined to create a pyramidal ridge directly above the stainless steel knife edge on the conflat flange. The machined gaskets were then annealed at 700°C in hydrogen making the copper soft to enable a vacuum tight seal. A schematic of the sample mounting is depicted in figure 2.

In a typical experiment, the desired temperature is established with both surfaces of the membrane under vacuum. The desired pressure of gas is accumulated upstream, behind a closed valve.

At time $t=0$, the membrane is rapidly exposed to the gas by opening the valve. The gas permeation rate as a function of time is monitored by the RGA. After an equilibrium permeation rate is established, the gas is rapidly removed from the upstream side of the membrane and the decline in permeation rate is recorded. The time-dependent data is used to determine the values of diffusivity, D and the steady state equilibrium flux is a direct measurement of the permeability constant, K . The RGA signal or sensitivity to the gas is converted into a flow rate by exposure to calibrated standard leak rates between tests.

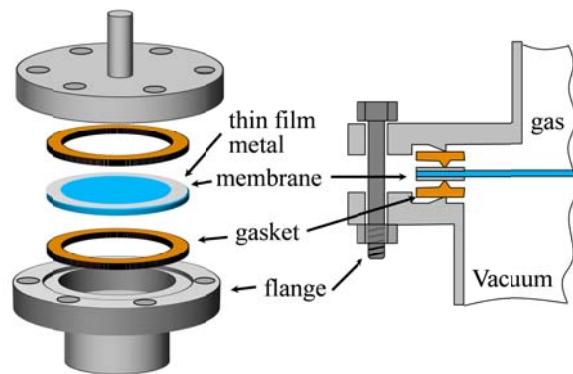


Figure 2 – Sample mounting configuration. The ceramic membrane is coated with silver on the perimeter and sealed between two soft copper gaskets.

Results and Discussion

A typical set of experimental permeation breakthrough data is shown in figure 3. The data in this plot is from a 1 mm thick LTCC sample at a temperature of 350°C. As can be seen, it took approximately 5 hours before any helium was detected on the vacuum side of the membrane and another three days were required to reach a steady state equilibrium helium permeation rate.

The process is reversed to remove the helium from the membrane, which requires an equal amount of time. A single permeability data point is collected in about one week from this representative data set. Values for the permeability constant K were determined by computationally fitting the experimental breakthrough data to equation (3). A

series expansion of this equation to $n=41$, was applied from which both K and D were determined. The permeation constant can also be calculated by applying equation (6) to the steady state equilibrium flux data. The diffusion constant could also be calculated by a time lag method described by Swets [6].

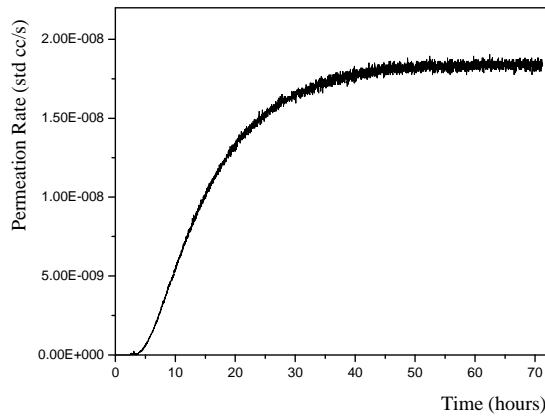


Figure 3 - Experimental breakthrough flux data

The temperature dependence of helium permeation through DuPont 951 LTCC was evaluated over a temperature range of 300°C to 450°C. To make measurements at low temperatures would require either thinner material or much longer measurement times. Figure 4 shows the log of the helium permeation constant plotted versus inverse temperature to make an Arrhenius style plot. Fitting the data to the Arrhenius equation, shown in equation (7) resulted in a pre-exponential factor of $K_0=3.17 \times 10^{-7}$ cm³(STP) cm/s cm² atm and an activation energy of $E_K=8.7$ kcal/mole.

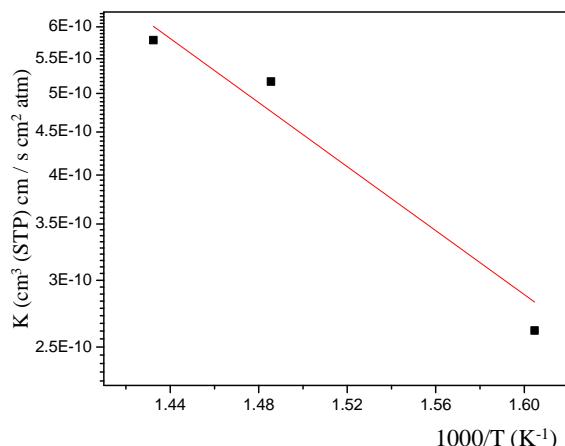


Figure 4 – Helium permeability as a function of temperature for DuPont 951

$$K = K_0 e^{\frac{-E_K}{RT}} \quad (7)$$

$$D = D_0 e^{\frac{-E_D}{RT}} \quad (8)$$

Values of the helium diffusion coefficient were also calculated over the temperature range of 300°C to 450°C. Figure 5 shows the log of the helium diffusion constant plotted versus inverse temperature to make an Arrhenius style plot. Fitting the temperature dependent diffusion data to equation (8), resulted in a pre-exponential factor of $D_0=6.28 \times 10^{-4}$ cm²/s and an activation energy of $E_D=12.4$ kcal/mole.

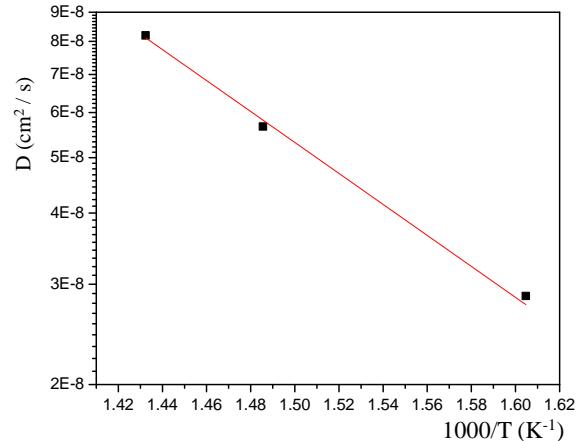


Figure 5 – Helium diffusion data as a function of temperature for DuPont 951

The solubility of helium in LTCC can be calculated from this data using equation (5) which shows that the permeability is equal to the diffusion multiplied by the solubility.

Figure 6 is a plot of the temperature dependence of the helium permeability constant for LTCC along with some glasses and ceramic materials for comparison. It should be noted that LTCC is comprised of alumina and 30 to 60% glass, according to the MSDS. Therefore it shouldn't be surprising that the measured value for permeability was found to be between the permeability of high purity alumina ceramics and glasses.

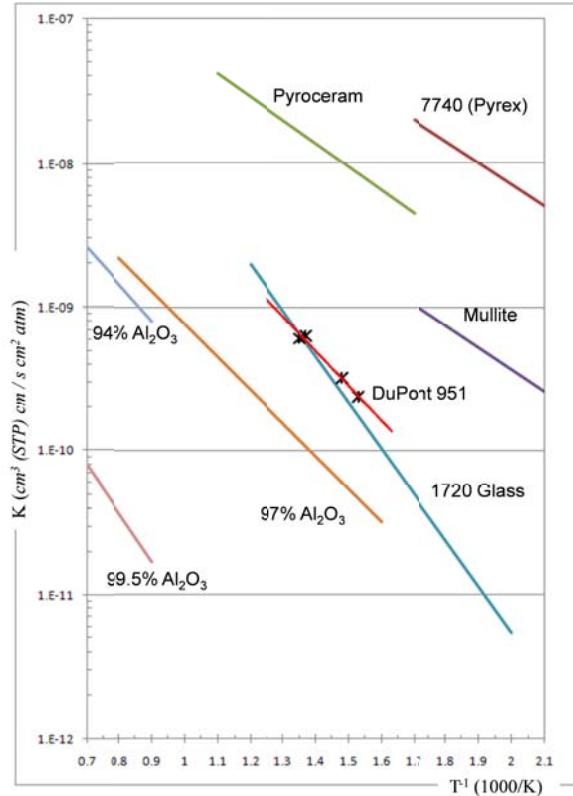


Figure 6 - Helium permeability through LTCC compared to a number of glasses and ceramics, reference data taken from [5].

Conclusion

The activation energy for helium permeation was found to be approximately 8.7 kcal/mole. The permeation data presented in this paper can be used for calculations of helium pressure inside LTCC vacuum packages as a function of lifetime. For example the helium permeability at 25°C is estimated to be 1×10^{-13} cm³(STP) cm/s cm² atm. Approximately 5.2 ppm of the atmosphere is helium, so a 1cm cubic LTCC vacuum package with 1 mm thick walls would have an internal helium pressure of $P=1 \times 10^{-4}$ Pa after one year. Helium permeation through DuPont 951 LTCC appears to be controlled by the glass phase. The addition of coatings, such as pure alumina, to the surface could have a significant impact on the helium permeation rate.

Acknowledgments

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