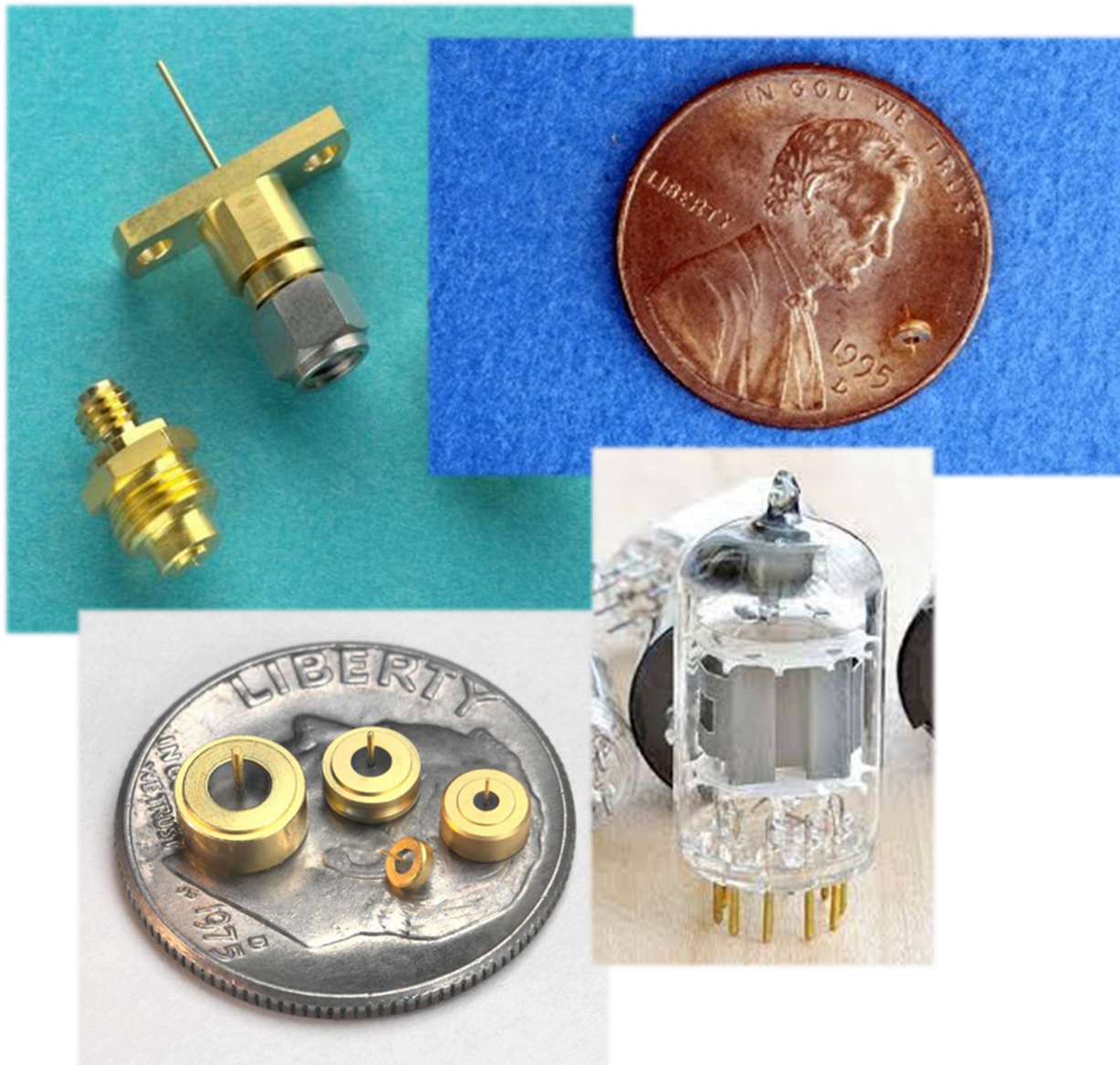


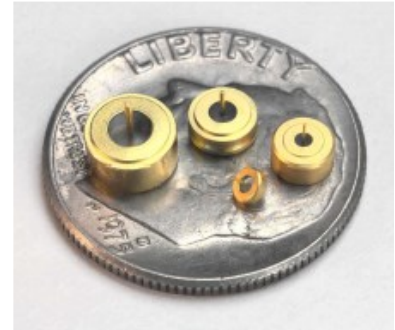
Controlled Expansion Alloys for Glass-to-Metal Sealing

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Since the Second World War, the evolution of precision coaxial connectors and accessories for high frequency microwave applications has driven a parallel development in the field of glass-to-metal seal (GMS) fabrication and a concurrent design and manufacturing trend toward smaller and more tightly toleranced components (see Fig. 1). The fundamental electrical performance of all hermetic coaxial connector designs, particularly in the mm-wave region, depends strongly on the precision of the glass-to-metal seal transition geometry. As the frequency range has pushed upward and concurrent glass seal geometries have become miniaturized, the resulting design requirements have stretched the limit of materials, metrology and manufacturing process technology. This article will present some of the fabrication and process development challenges associated with glass-to-metal seal technology and the use of controlled expansion alloys in their design.



The fundamental electrical performance of hermetic precision coaxial connectors in the mm-wave regime is critically dependent on the precision of the GMS transition geometry. If one considers the following equation, which defines the cutoff frequency for a coaxial transmission line,

$$f_c = 7512 / \sqrt{\epsilon (d + D)} \quad (\text{Eq. 1})$$



where ϵ is the dielectric constant in the transmission line, d is the outer diameter of the center conductor, and D is the inner diameter of the outer conductor, it is clear that f_c increases as the characteristic dimensions of the coaxial line decrease. For the case of the 1.0 mm GMS (see Fig. 2), named for the nominal inner diameter dimension of the sleeve (D in Equation 1), the corresponding dimension of the center pin (d in Equation 1) is 150 microns, or about twice the diameter of an average human hair. For these miniature geometries, conventional machining tolerances represent a relatively large percentage of a particular component's size. And since the skin depth for signal transmission above 100 GHz is on the order of a half micron, the components of the 1.0 mm GMS must display microscopically smooth surface finishes. Considering the additional complications in fixturing, assembly and metrology, it will be appreciated that fabrication of glass seals for high frequency microwave applications represents a formidable manufacturing challenge.

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But before proceeding with a discussion of glass-to-metal seal designs and processing, I feel it is instructive to review the thermodynamic principles on which the technology depends, namely the Young Equation and how it defines the wetting behavior of a liquid/solid interface. The distinct lack of thermodynamic affinity between glasses and metal alloys is the primary reason that joining of these materials has historically resulted in considerable technical complexity. The degree to which a liquid phase will wet a solid it is in physical contact with, within a vapor/liquid/solid three phase system, is a direct consequence of the particular conditions of thermodynamic equilibrium. By balancing the horizontal components of the interfacial energies (surface tensions) at the point of contact of such a three phase system (see Figure 3), Thomas Young expressed this “mechanical” relationship at the turn of the last century in his

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (\text{Eq. 2})$$

where γ_{sv} is the interfacial energy between the solid and vapor, γ_{sl} is the interfacial energy between the solid and liquid, γ_{lv} is the interfacial energy between the liquid and vapor, and θ is the liquid/solid contact angle measured inside the sessile liquid drop. For the case depicted in Fig. 3, $\gamma_{sv} > \gamma_{sl} > \gamma_{lv}$ so that the contact angle θ is acute, and by definition wetting of the solid by the liquid occurs. However, for the case where $\gamma_{sv} < \gamma_{sl} < \gamma_{lv}$, the contact angle is obtuse and wetting of the solid by the liquid is thermodynamically unfavorable. The second case is typical of liquid glass in contact with a metal alloy substrate.

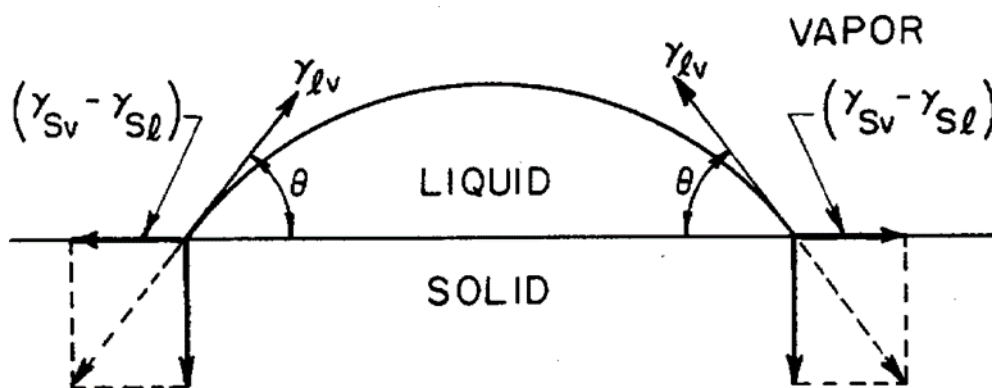
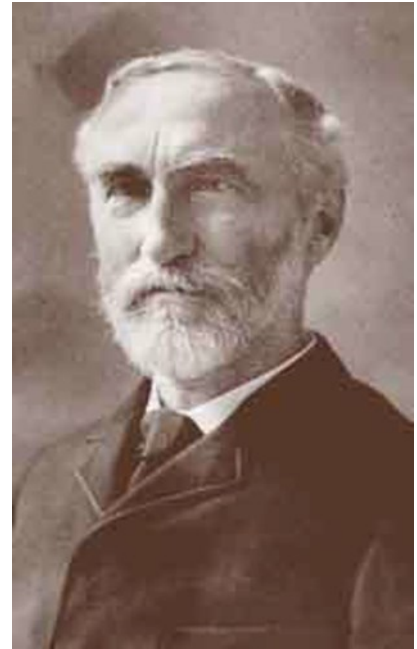


Fig. 3 – Sessile drop configuration.

(Courtesy J. Pask and A. Tomsia)

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Toward the end of the nineteenth century, J.W. Gibbs (Fig. 4) presented a more rigorous thermodynamic treatment of Young's construction. Although he accounted for the effects of a gravitational field on the system, like Young he assumed the system to be at chemical equilibrium with no mass transport across the interfaces. By now it is well established that the effect of chemical reactions on the relative interfacial energies of solid/liquid/vapor three phase systems, particularly at elevated temperatures where mass transfer effects can be significant, is such that the free energy of the reaction can enhance the driving force for wetting of the solid by the liquid. This is true because mass transfer across the interfaces must result in a net decrease of the free energy of the system at any time, otherwise the reaction would not proceed. In effect, the magnitude of the relative interfacial energy between the solid and the liquid (γ_{sl}) is decreased by chemical reactions at the interface, so that the driving force for wetting of the solid and spreading by the liquid is improved.



**Fig. 4 – Josiah Willard Gibbs
1839 - 1903**

The basic requirements for strong, hermetic glass-to-metal seals are chemical bonding (i.e. electronic structure via atomic contact) and minimal stress differentials at the interfaces with favorable stress gradients in the interfacial zones. It can be generalized that any two phases will form chemical bonds if they are at stable chemical thermodynamic equilibrium at their interface whether or not the bulk phases are at equilibrium, providing they are also compatible physically. Although it is well known that stress differentials at GMS interfaces are minimized by matching the thermal expansion coefficients of the components, the dependence of stress gradients in the interfacial zones on composition gradients that form during the fusing of the seals is not as well recognized.

The technological procedure for achieving chemical bonding and favorable stress gradients in GMS assemblies is to first pre-oxidize the metallic alloy components. If the resulting metal oxide is of proper thickness and composition, when the GMS is fused at temperature the molten glass

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will wet and dissolve the oxide. The glass at the oxide interface immediately becomes saturated because the solution rate of the oxide is faster than the diffusion rate of the dissolved oxide into the bulk glass. In this way chemical bonding is realized. The oxide layer also bonds chemically to the metal, which is saturated with the oxide, at least at the metal/oxide interface.

As the dissolved oxide diffuses into the glass, a concentration gradient is formed that becomes more extended with time. The presence of the dissolved metal oxide in the molten glass affects its coefficient of thermal expansion because of an increase in the O/Si ratio and the introduction of cations with different degrees of covalency. The concentration gradients are then proportional to thermal expansion coefficient gradients, which generally results in more favorable stress gradients.

Hence, the saturation of the glass with metal oxide near the interface and the subsequent diffusion of the oxide into the bulk of the glass result in chemical bonding and favorable stress gradients as required. In effect, the metal oxide serves to act as a "thermodynamic glue."

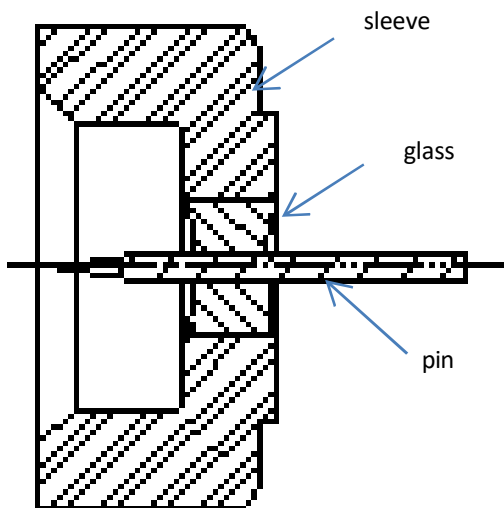


Fig. 5 – Glass-to-metal seal components.

Although a number of classification schemes have been developed for glass-to-metal seals (Fig. 5), such as those based on function or geometry, the most direct and succinct is a classification based on the thermal expansion (i.e. residual stress) relationship of the glass seal components. As such, glass-to-metal seal types can be categorized as matched seals, compression seals, and what will be referred to as hybrid seals.

For matched glass-to-metal seals, the component materials for the sleeve, pin and glass are selected so their thermal expansion characteristics are relatively close to each other throughout the sealing temperature range. As a rule of thumb, this means the average coefficient of thermal expansion (CTE – expressed in units of $\text{cm}/\text{cm } ^\circ\text{C}$ or simply $1/^\circ\text{C}$) for the glass and metal are within about 5 parts per million of each other. The strength of matched seals relies on chemical bonding developed during the sealing process between the glass and a metal oxide that has previously been grown on the metal components. An example of

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material selection for a matched glass-to-metal seal is borosilicate glass (CTE – $4.7 \times 10^{-6}/^{\circ}\text{C}$) and ASTM F-15 controlled expansion alloy (Kovar[®], CTE - $5.3 \times 10^{-6}/^{\circ}\text{C}$) for the sleeve and pin. Depending on the glass type selected, alternative controlled expansion alloys include Alloy 42[®] (CTE – $7.0 \times 10^{-6}/^{\circ}\text{C}$), Alloy 46[®] (CTE - $7.9 \times 10^{-6}/^{\circ}\text{C}$) or Alloy 48[®] (CTE - $9.0 \times 10^{-6}/^{\circ}\text{C}$).

Compression glass-to-metal seals are designed such that the sleeve or housing material has a thermal expansion coefficient that is significantly higher than the glass and pin, particularly below the set point (often referred to as the softening point) temperature of the glass. Typically, the difference in CTE between the glass and housing for compression seals is 5-10 parts per million, depending on seal geometry and material selection. During the sealing process, the housing contracts around the solidified glass and puts the glass under a compressive stress. This is advantageous because the compressive strength for most glasses is about an order of magnitude higher than the tensile strength, which imparts considerable mechanical stability to the glass seal assembly. In practice, the thermal expansion hierarchy for the components is designed such that the CTE of the housing is at least 5 ppm greater than the glass, and the glass CTE is slightly higher than the pin. This approach insures that the various glass-metal interfaces remain under compression when the glass seal is subjected to thermal cycling in service. An example of materials for a hierarchical compression seal is 316 stainless steel (CTE – $18.5 \times 10^{-6}/^{\circ}\text{C}$) for the housing, soda-barium glass (CTE – $9.5 \times 10^{-6}/^{\circ}\text{C}$) and ASTM F30 alloy (Alloy 52[®], CTE – $9.9 \times 10^{-6}/^{\circ}\text{C}$) for the pin.

The hybrid glass-to-metal seal combines the attributes of a compression seal and a matched seal in the same construction. The component materials are selected so that the hierarchy in their CTEs insures the glass in the seal will be under compression at room temperature. The metal alloy materials are selected so that it is possible to preoxidize the sleeve and pin prior to glass fusing and as such, realize chemical bonding at the metal/glass interfaces. An example of materials for a hybrid seal is AISI 1215 steel (CTE – $12 \times 10^{-6}/^{\circ}\text{C}$) for the sleeve, borosilicate glass (CTE – $4.7 \times 10^{-6}/^{\circ}\text{C}$) and ASTM F-15 alloy (CTE – $5.3 \times 10^{-6}/^{\circ}\text{C}$) for the pin. For matched and hybrid glass-to-metal seal assemblies, tungsten (CTE – $4.6 \times 10^{-6}/^{\circ}\text{C}$) and molybdenum (CTE – $5.5 \times 10^{-6}/^{\circ}\text{C}$) are sometimes utilized for the center pin material.

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The general process sequence for fabrication of glass-to-metal seal assemblies involves a number of separate steps. First, the components (glass, center pin and sleeve or housing) must be thoroughly cleaned. For the metal alloy components, this usually starts with degreasing in a solvent to remove residual machining oils or coolants followed by a light acid etch, such as dilute HCl, to remove undesirable oxides (e.g. rust). Generally, the glass beads do not require more than rinsing in a mild solvent, such as isopropyl alcohol, to eliminate particulate left behind after the forming operation. This is true for glass preforms produced using glass frit (powder) that is mixed with a binder and pressed into the final shape or fabricated from drawn glass tubing, from which the glass preforms are sawed to length.

The metal components (sleeve and pin) are out gassed, to drive off occluded gasses that are sometimes entrained during the alloy manufacturing process, and then decarburized. Because of the relatively high processing temperature involved, out gassing of the metal parts occurs naturally when the decarburization process is performed. The presence of carbon in the sealing alloy is detrimental because carbon will react with oxygen in the glass to form CO and CO₂ bubbles at the glass/metal interface, during the glass fuse operation. These bubbles are detrimental because they can lead to blistering and loss of adherence at the interface. Decarburization can be achieved by exposing the parts to a moist hydrogen atmosphere with a dewpoint of about 20° C at 1000-1100° C for 7-15 minutes, depending on the size of the part. The key, particularly with Kovar®, is to select the decarburization temperature so that it is higher than the glass sealing temperature.

For the case of matched, hybrid and sometimes the center pin for compression seals, the next step is to grow a contiguous intergranular oxide layer on the metallic components. The preoxidation procedure is critical to the ultimate reliability of glass seals that rely on chemical bonding, so process control is paramount. If the oxide is too thin, the strength of the glass-to-metal interface will be low due to superficial chemical bonding. Conversely, excessive oxide thickness may compromise the hermeticity and strength of the seal due to porosity in the oxide or bubbles that can form when the glass is fused. The preoxidation process is typically conducted in a controlled atmosphere belt furnace using a moist nitrogen environment (sometimes augmented with 0.25-0.5% hydrogen) at a dewpoint of 3-9° C and a set point temperature of 850-1050° C. The optimal residence time depends on the mass of the parts and the particular furnace parameters, but is usually on the order of 4-7 minutes.

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After the GMS components have been cleaned, out gassed, decarburized and preoxidized, they are assembled into tooling fixtures for the glass sealing step. Graphite is the most common material used for glass fuse tooling, especially for tooling that comes in direct contact with the glass, because graphite can be machined to very close tolerances and molten glass does not wet or stick to it (due to the interfacial energy relationship). The sealing process is performed in a continuous furnace under dry nitrogen (dewpoint < -20° C) or a lean exothermic gas atmosphere at temperatures ranging from 950-1000° C for 15-30 minutes, depending on the mass of the fixtures and oxide thickness on the parts. A dry nitrogen atmosphere is beneficial because it mitigates decomposition of the carbon tooling and possible unwanted oxidation of stainless steel compression seal components, which can occur in the presence of even small amounts of moisture. Ideally, matched and hybrid seals should emerge from the fuse furnace with minimal oxide remaining on their free surfaces, to facilitate the subsequent chemical cleaning necessary to remove the residual oxide prior to the electroplating step. In most cases the fused glass-to-metal seals are electroplated, typically with several microns of gold over a diffusion barrier of nickel, to facilitate solder and lead termination processes that occur when the glass seals are incorporated into upper level assemblies.



Fig. 6 – 1 mm connectors with integral glass-to-metal seals.

We have reviewed the chemical and physical factors that lead to strong, hermetic glass-to-metal seals and how controlled expansion alloys can be effectively employed in GMS design. The achievement of equilibrium chemical bonding at all interfaces and development of acceptable stress patterns and gradients across the interfacial zones is vital. Favorable stress patterns are dependent on relative CTE matching of the components and composition gradients and microstructures that form because of reactions at the interfaces and diffusion of metal oxide into the bulk glass. Understanding the first principles involved in glass-to-metal sealing encourages design advances in R&D and better control in manufacturing.