**Title:** GLASS/CERAMIC SEALING SYSTEM

The present invention relates to a glass/ceramic sealing system (54). A sealing glass (54) having a coefficient of thermal expansion in excess of $160 \times 10^{-7} \text{ cm/cm}^\circ\text{C}$ is provided. The glass is useful for matched sealing of copper and copper based alloys (52). The glass (54) is capable of ceramization, greatly increasing the resistance of the glass to moisture penetration and fracture due to mechanical damage. The temperature of ceramization has been designed so that a solutionized copper alloy leadframe (20) is age hardened during ceramization. The glass has particular utility in the manufacture of electronic packages (12) and multi-layer circuitry.
<table>
<thead>
<tr>
<th>Code</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT</td>
<td>Austria</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
</tr>
<tr>
<td>DE</td>
<td>Germany, Federal Republic of</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
</tr>
<tr>
<td>GA</td>
<td>Gabon</td>
</tr>
<tr>
<td>GB</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>HU</td>
<td>Hungary</td>
</tr>
<tr>
<td>IT</td>
<td>Italy</td>
</tr>
<tr>
<td>JP</td>
<td>Japan</td>
</tr>
<tr>
<td>KP</td>
<td>Democratic People's Republic of Korea</td>
</tr>
<tr>
<td>KR</td>
<td>Republic of Korea</td>
</tr>
<tr>
<td>LJ</td>
<td>Liechtenstein</td>
</tr>
<tr>
<td>LK</td>
<td>Sri Lanka</td>
</tr>
<tr>
<td>LU</td>
<td>Luxembourg</td>
</tr>
<tr>
<td>MC</td>
<td>Monaco</td>
</tr>
<tr>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>SU</td>
<td>Soviet Union</td>
</tr>
<tr>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>US</td>
<td>United States of America</td>
</tr>
</tbody>
</table>
GLASS/CERAMIC SEALING SYSTEM

This invention relates to a glass-ceramic sealing systems. The coefficient of thermal expansion of the sealing system may be matched to that of copper and copper based alloys. The sealing system is further strongly resistant to moisture penetration and to fracture due to mechanical shock. The sealing system is particularly useful to bond metal electronic packages as well as electrical connectors.

There are many metal-glass-ceramic applications and systems which have in common the bonding of a glass or ceramic material to the surface of a metal. One common application is in the manufacture of hermetic packages designed to enclose electronic devices such as silicon semiconductor devices.

Perhaps the most common hermetic package is the ceramic dual in line package commonly known as the CERDIP. The package contains a base component and a cover component made of aluminum oxide. The components are joined together, frequently with a metal leadframe disposed between, by a sealing glass. The glass is fabricated to have a coefficient of thermal expansion approximating that of the aluminum oxide components, about $49 \times 10^{-7} \text{cm/cm/}^\circ\text{C}$.

As semiconductor technology developed, the electronic devices became more complex. More electronic circuitry was positioned on smaller surface areas and as a result, the electronic device generated more heat during operation. Aluminum oxide has insufficient thermal conductivity to prevent the device from
overheating so alternatives to the CERDIP were developed.

Among the alternatives was the metal package. A metal or metal alloy replaced the aluminum oxide as the base and cover components of the package. Initially, low expansion alloys such as the iron-nickel-cobalt alloy known by the tradename KOVAR or low expansion metals such as molybdenum were used. Sealing glasses used for sealing CERDIP packages were adapted to the metal packages. To increase adhesion of the glass to the metal components, a thin layer of a metal oxide was formed on the surface of the base and cover components in accordance with technology known from the fabrication of glass to metal seals for the vacuum tube industry.

A glass suitable for bonding to molybdenum (coefficient of thermal expansion = 49 x 10^{-7} cm/cm/°C) containing SiO₂, Al₂O₃, MgO, ZrO₂, TiO₂ and Li₂O is disclosed in U.S. Patent 3,473,999 to Mochow.

As semiconductor devices continued to increase in complexity, the need for package components with improved thermal conductivity also increased. Typically, there is a correlation between the thermal conductivity and the coefficient of thermal expansion of a material. As the thermal conductivity increases, the coefficient of thermal conductivity likewise increases. Therefore, the higher thermal conductivity electronic packages require a sealing glass with a higher coefficient of thermal expansion.

A sealing glass for stainless steel having a coefficient of thermal expansion of 120 x 10^{-7}
- 140 \times 10^{-7} \text{ cm/cm/°C} containing SiO\textsubscript{2}, K\textsubscript{2}O, Na\textsubscript{2}O, Al\textsubscript{2}O\textsubscript{3} and MgO is disclosed in U.S. Patent No. 3,804,703 to Hirayama.

A sealing glass for nickel having a coefficient of thermal expansion of about 150 \times 10^{-7} \text{ cm/cm/°C} and containing SiO\textsubscript{2}, Na\textsubscript{2}O, K\textsubscript{2}O, a mixture of (BaO,SrO and CaO) and Al\textsubscript{2}O\textsubscript{3} is disclosed in U.S. Patent No. 2,948,992 to Oldfield. Yet another relatively high expansion glass is known by the tradename CORNING 1990 and sold by Corning Glass Works located in Corning, New York. This glass contains SiO\textsubscript{2}, Li\textsubscript{2}O, Na\textsubscript{2}O, K\textsubscript{2}O and PbO and has a coefficient of thermal expansion of about 136 \times 10^{-7} \text{ cm/cm/°C}.

To maximize thermal conductivity, package components made from copper or copper base alloys are preferred. The coefficient of thermal expansion of these materials is in the range of from about 160\times10^{-7} to about 180\times10^{-7} \text{ cm/cm/°C}. Glasses with coefficients of thermal expansion in the same range were required.

Glasses have been developed which are close to the coefficient of thermal expansion of copper. For example, U.S. Patent No. 3,407,091 to Busdiecker discloses a glass containing Al\textsubscript{2}O\textsubscript{3}, K\textsubscript{2}O, ZnO and P\textsubscript{2}O\textsubscript{5} for sealing to copper or copper alloys. The coefficient of thermal expansion of this glass was measured to be 141\times10^{-7} \text{ cm/cm/°C}. However, if the mismatch between the glass and the substrate is much greater than about 10\%, it has been found the glass will develop microcracks and hermeticity of the package will be lost.

Sealing glasses with coefficients of thermal expansion approximating that of copper
have been made by adding a filler with a high
coefficient of thermal expansion, such as
calcium fluoride, to a sealing glass. U.S.
Patent No. 4,185,139 to Sermos as well as U.S.
Patent Nos. 4,775,647 and 4,818,730 to Smith
discloses the use of a filler.

A problem with a filler is excessive
amounts of filler lead to a deterioration of the
rheological properties and can affect seal
integrity. Also, as the sealing glass is
heated, some of the filler is dissolved.
Dissolution of filler may lead to outgassing.
One approach to the problem of excessive
dissolution is coating the filler as shown in
U.S. Patent No. 4,185,139 to Sermos. However,
coating is difficult and does not solve the
problem of excessive filler.

A homogeneous sealing glass which has a
coefficient of thermal expansion matching that of
copper and copper based alloys which does not require
the addition of a filler consists essentially of at
This sealing glass consists essentially of at
least fifty molar percent SiO₂; from about ten
to about twenty molar percent BaO; from about
twenty to about thirty molar percent of an
alkaline oxide component, the alkaline oxide
component is comprised of at least two alkaline
oxides selected from the group consisting of
Na₂O, K₂O and Li₂O; up to about five molar
percent Al₂O₃; and up to ten molar percent of an
additive.

In accordance with the present invention, a
sealing system comprising a glass-ceramic
material is provided. The glass-ceramic has a coefficient of thermal expansion approximately matching that of copper or copper based alloys. The sealing material is supplied as a glass and is capable of ceramization. Ceramization is the nucleation and growth of one or more crystalline phases from a non-crystalline matrix. The glass-ceramic exhibits improved resistance to moisture as well as chemical corrosion. It is further more resistant to mechanical shock than conventional sealing glasses.

The glass-ceramic of the invention is a homogeneous mixture consisting essentially of the following elements in approximately the following ratio:

<table>
<thead>
<tr>
<th>Element</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>at least about 40 molar percent.</td>
</tr>
<tr>
<td>BaO</td>
<td>from about 5 molar percent to about 25 molar percent</td>
</tr>
<tr>
<td>alkaline oxide</td>
<td>combination of at least two, the combination being from about 15 molar percent to about 45 molar percent.</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>from about 0.1 molar percent to about 5 molar percent.</td>
</tr>
<tr>
<td>ZnO</td>
<td>up to about 15 molar percent.</td>
</tr>
<tr>
<td>PbO</td>
<td>up to about 10 molar percent.</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>up to about 5 molar percent.</td>
</tr>
</tbody>
</table>
additives up to about 10 molar percent.

The glass is sealed at temperatures of from about 780°C to about 850°C without deterioration. High temperature stability permits the assembly of age hardenable copper alloy packages which may be thermally treated subsequent to sealing. Following glass sealing, the glass is partially converted into a ceramic by heat treating at a temperature of from about 550°C to about 750°C. After ceramization, it is preferable to anneal the glass-ceramic at a temperature of from about 350°C to about 500°C. In one embodiment, the copper alloy packaging components are selected to be age hardenable during the glass-ceramic annealing step.

It is an object of the present invention to provide a sealing system having a coefficient of thermal expansion approximately equal to that of copper or a copper based alloy.

It is another object of the invention to provide a sealing system having improved moisture resistance.

It is another feature of the invention to provide a sealing system having improved resistance to mechanical shock.

It is a feature of the invention that the glass is homogeneous and free of undissolved or partially dissolved fillers.

It is another feature of the invention that the sealing system comprises a sealing glass capable of ceramization.

It is a feature of the invention that the glass has a sealing temperature of about 800°C
and is suitable for the sealing of metal or metal alloy packages designed to house electronic devices.

It is an advantage of the present invention that the glass crystallizes at a temperature suitable for age hardening the metal alloy components.

Accordingly, there is provided a ceramicizable sealing glass having a coefficient of thermal expansion approximately matching that of copper or copper based alloys. The glass-ceramic is annealed at a temperature which promotes age hardening of precipitation hardenable copper alloys. The glass-ceramic is particularly suitable to bond copper or copper alloy components of hermetic electronic packages.

These and other advantages will become more apparent from the following description and drawings.

Figure 1 shows in cross section an electronic package manufactured in accordance with the invention.

Figure 2 shows in cross section a glass-metal composite material manufactured in accordance with the invention.

Figure 3 shows in cross section a multi-layer circuit manufactured in accordance with the invention.

The invention relates to sealing glasses capable of ceramization. The glasses are characterized by a coefficient of thermal expansion approximately matching a metal or
metal alloy, preferably that of copper or a copper based alloy. Preferably, the coefficient of thermal expansion is in the range of from about 160×10⁻⁷ cm/cm/°C to about 180×10⁻⁷ cm/cm/°C and, most preferably, in the range of from about 165×10⁻⁷ cm/cm/°C to about 175×10⁻⁷ cm/cm/°C.

The glasses are further preferably homogeneous, that is, without any undissolved fillers or other media present.

The glasses are preferably sodium free which has been found to improve moisture resistance.

In a preferred composition, the glass contains SiO₂, BaO, LiO₂, K₂O, K₂O, and V₂O₅.

The glass is predominantly comprised of silicon dioxide, at least about 40 molar percent. More preferably, the concentration of SiO₂ is from about 40 molar percent to about 50 molar percent and, most preferably, the concentration is from about 45 molar percent to about 48 molar percent.

The barium oxide component is preferably present in concentrations of from about five molar percent to about twenty five molar percent. Barium oxide is a major contributor to the thermal expansion coefficient of the glass composite. The desired concentration of BaO is determined by the coefficient of thermal expansion of the metal alloy which is being sealed. For most copper or copper based alloys, a BaO concentration of from about ten molar percent to about twenty molar percent is preferred. Twelve to about fifteen molar percent is most preferred.
A combination of alkaline oxides is added to the glass. These alkaline oxides increase the coefficient of thermal expansion of the glass as well as improve moisture resistance. Preferred alkaline oxides are lithium oxide and potassium oxide. Other suitable alkaline oxides are Rb₂O₃ and Cs₂O₃. Sodium oxide (Na₂O₃) is not preferred as the inclusion of greater than about 5 molar percent of this oxide makes the glass susceptible to moisture penetration.

Lithium oxide is preferable supplied in a concentration of from about 5 molar percent to about 15 molar percent and most preferably in a concentration of from about 6 molar percent to about 9 molar percent.

Potassium oxide is supplied in a preferred concentration of from about 10 molar percent to about 30 molar percent and most preferably in a concentration of from about 18 molar percent to about 22 molar percent.

A final constituent of the sealing glass is a nucleating agent, preferably vanadium oxide (V₂O₅). Vanadium oxide has been found to improve the adhesion of the sealing glass to the metal alloy substrate and further acts as a nucleating site to promote ceramization.

The preferred concentration of vanadium oxide is in the range of from about 0.1 molar percent to about 5 molar percent. The most preferred concentration of vanadium oxide is in the range of from about 0.3 molar percent to about 0.8 molar percent.

Phosphorous oxide (P₂O₅) in about the same concentrations as the vanadium oxide has also been found to act as a nucleating agent to
promote ceramization.
Certain additives including lead oxide (PbO), zinc oxide (ZnO) and aluminum oxide (Al₂O₃) are desirable. Lead oxide adjusts the melting point of the sealing glass. Increasing the concentration of lead oxide decreases the sealing temperature of the glass. The oxide has been found to increase the moisture resistance of the residual matrix. The lead oxide concentration is preferably in the range of up to about 10 molar percent. A most preferred concentration is from about 4 molar percent to about 6 molar percent. The concentration is preferably kept below about 6 molar percent.
Sealing glasses containing higher concentrations of lead oxide often require an oxidizing atmosphere for sealing. The choice of copper alloy substrates for the metal package often mandates sealing in a reducing or neutral atmosphere.
Zinc oxide both improves the moisture resistance of the residual glass phase and facilitates the precipitation of the crystalline ceramic phase. The concentration of the zinc oxide additive is preferably up to about 15 molar percent. A most preferred zinc oxide concentration is in the range of from about 6 molar percent to about 8 molar percent.
Preferably, a small amount of aluminum oxide is also added to the glass. It has been found that aluminum oxide increases the chemical resistance of the residual glass phase. Aluminum oxide lowers the coefficient of thermal expansion of the sealing glass. It is preferred to maintain the aluminum oxide concentration to
less than about 5 molar percent. Most preferably, the Al$_2$O$_3$ concentration is from about 1 molar percent to about 3 molar percent.

Various other additives may be combined with the glass, generally in concentrations of less than about 10 molar percent. Additives which may be combined with the sealing glass include, but are not limited to B$_2$O$_3$, CaO, Ni$_2$O, TiO$_2$ and SrO.

As an illustrative example, which is not intended to limit the invention, the following sealing glass composition has been found to give a coefficient of thermal expansion of 167$x10^{-7}$ cm/cm/°C. The sealing glass readily precipitates a ceramic phase upon heat treating. The resulting glass-ceramic is characterized by good chemical and moisture resistance as well as resistance to fracture resulting from mechanical shock.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Molar %</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>45.9</td>
<td>31.64</td>
</tr>
<tr>
<td>PbO</td>
<td>4.6</td>
<td>11.78</td>
</tr>
<tr>
<td>BaO</td>
<td>13.0</td>
<td>22.87</td>
</tr>
<tr>
<td>ZnO</td>
<td>7.2</td>
<td>6.72</td>
</tr>
<tr>
<td>Li$_2$O</td>
<td>7.3</td>
<td>2.5</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>19.1</td>
<td>20.64</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.4</td>
<td>2.81</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>0.5</td>
<td>1.04</td>
</tr>
</tbody>
</table>

The glass is formed by combining the proper ratio of desired source materials. The source materials which are usually the oxides or carbonates of the desired elements are generally
supplied in powder form with a particle size of about 5 microns. The dry powders are mixed well, for example by vibratory mixing to insure a homogeneous glass. The powder mixture is then heated to a temperature in the range of from about 1300°C to about 1500°C and most preferably at a temperature of from about 1325°C to about 1375°C.

The molten glass is cooled to room temperature rapidly, as by a water quench. The glass is reduced to a powder having a particulate size of from about 5 microns to about 10 microns by a process such as attrition.

The glass powder is mixed with an organic solvent such as terpinol to facilitate application of the sealing glass to a substrate. Application of the glass/solvent mixture is frequently done by screen printing although any process known in the art is acceptable.

The glass/solvent is then glazed by heating to a temperature of from about 600°C to about 750°C in air for a time in the range of from about 15 minutes to about 30 minutes. Glazing evaporates the binder as well as causes glass particulate to sinter and loosely bond to adjoining glass particulate as well as to the metal substrate.

Following glazing, the glass is sealed. Glass sealing is at a temperature above about 750°C and most preferably in the range of from about 780°C to about 850°C. The high temperature of glass sealing results in solutionizing of precipitation hardenable components of a metal package or other device being bonded. Solutionizing is when the alloy
precipitates dissolve into the copper matrix producing a soft, ductile material. For example, after glass sealing a precipitation hardened leadframe would be in the solutionized state and may be easily bent to a desired radius. The more easily the leadframe may be bent, the less likely damage to the glass seal during lead bending. Prebent leadframes, in which the leads are bent to a desired radius prior to glass sealing may also be used.

The glass is next subjected to a ceramization step. Ceramization is the nucleation and growth of one or more crystalline phases from a non-crystalline matrix. Crystallization may be initiated by subjecting the glass to a heat treatment in the range of from about 550°C to about 750°C for a time in the range of from about 15 minutes to about 90 minutes. Most preferably, the ceramization step occurs at from about 600°C to about 650°C for a time of from about 20 minutes to about 40 minutes. This time and temperature range is particularly desirable. The preferred precipitation hardenable copper alloys age in the same temperature and time range. When a solutionized precipitation hardened alloy ages, an alloy component precipitates from the copper matrix producing the precipitation hardened alloy. For example, a solutionized leadframe manufactured from copper alloy CDA 724 has a tensile strength of 413 MPa (60 ksi) and may be easily bent. After aging, the same leadframe has a tensile strength of 680 MPa (100 ksi) and is resistant to bending from handling.

The use of precipitation hardened copper
alloys as package components has been disclosed in United States Patent No. 4,805,009 by Prior et al. The use of a precipitation hardenable copper alloy leadframe which is assembled in a package in the solutionized state and then age hardened during glass sealing is disclosed in PCT Application PCT/US88/00019, published July 14, 1988.

It is desirable to anneal the glass-ceramic after ceramization. A preferred annealing process is to heat the glass-ceramic to a temperature of from about 350°C to about 450°C for a time of from about 15 minutes to about 45 minutes. A most preferred annealing process is to heat the glass to a temperature of from about 390°C to about 420°C for about 25 minutes to about 35 minutes.

The advantages of this glass-ceramic sealing system will become more apparent from the following examples demonstrating the use of the system in electronic devices.

# EXAMPLE 1

The preferred glass has a sealing temperature in excess of about 750°C. Elevated sealing temperature glasses are particularly suited for the manufacture of "window frame" packages as described hereinbelow.

Figure 1 illustrates in cross section a hermetic metal package 10 adapted to house an electronic device 12, usually a silicon based semiconductor. Hermetic metal packages are disclosed in U.S. Patent No. 4,524,238 to Butt and U.S. Patent No. 4,656,499 to Butt.
The package 10 is comprised of a base component 14, a window frame 16 and a cover component 18. A leadframe 20 is disposed between the window frame 16 and base component 14 and serves to electrically connect the electronic device 12 to external circuitry.

While metal or metal alloys may be used to manufacture the package components, copper alloys which form refractory oxides are preferred. Alloys which form a surface refractory oxide when heated in an oxidizing atmosphere are referred to herein as alloys which form a glass sealable layer "in situ".

Other alloys may be coated with a glass sealable oxide forming metal or metal alloy by cladding. Plating, vapor deposition or sputtering as disclosed in U.S. Patent No. 4,796,083 by Cherukuri et al may also be used. The process is referred to herein as forming a glass sealable layer by an "additive" process.

Preferred copper alloys include alloys 638, 724 and 7025. Alloy 638 contains 2.5-3.1% aluminum, 1.5-2.1% silicon and the balance copper as described in U.S. Patent Nos. 3,341,369 and 3,475,227 issued to Caule et al. A refractory oxide layer formed substantially of aluminum oxide (Al\(_2\)O\(_3\)) may be produced by any desired method. For example, the alloy may be preoxidized by heating to a temperature of between about 330°C and 820°C in gases having an extremely low oxygen content such as 4%
hydrogen, 96% nitrogen and a trace of water.

Alloy C638 may not be preferred for all packaging applications. The alloy anneals at glass sealing temperatures and the assembled package is subject to distortion and damage due to its softened state. A more preferred alloy is a precipitation hardened alloy suitable for glass sealing such as copper alloy C724.

Alloy C724 consists essentially of from about 10% to about 15% nickel, from about 1% to about 3% aluminum, up to about 1% manganese, from about 0.05% to less than about 0.5% magnesium and the balance copper as disclosed in U.S. Patent No. 4,434,016 to Saleh et al.

The use of alloy C724 as well as other precipitation hardened alloys for leadframes in glass sealed metal packages is disclosed in U.S. Patent No. 4,704,626 to Mahulikar.

Another preferred copper based alloy, C7025, consists essentially of from about 2 to about 4.8 weight percent nickel, from about 0.2 to about 1.4 weight percent silicon, from about 0.05 to about 0.45 weight percent magnesium and the balance copper. Alloy C7025 is disclosed in U.S. Patent No. 4,594,221 to Caron et al. Alloy C7025 achieves maximum hardness when aged at a temperature of about 450°C for about 2 hours.

Precipitation hardenable alloys are referred to as being in the solution treated or homogeneous state when they are single phase. Solutionized alloys are rather ductile. When the alloys are in the precipitation or age hardened state, they are multi-phase and less
ductile. By controlled heating and cooling, an alloy may be transformed from solution treated to age hardened or from age hardened to solution treated.

The glass of the present invention seals at temperatures above 750°C so a precipitation hardenable leadframe may be glass sealed in the solution treated state, bent to a desired shape, and then age hardened without the properties of the glass being degraded.

Nothing in the above is intended to limit the package components to precipitation hardened alloys or to a single alloy. For example, the base component 14 may be comprised of oxygen free (OFHC) copper or a dilute copper alloy such as alloy C194 (1.5% - 3.5% iron and small amounts of zinc or mixtures of zinc and phosphorous and the balance copper as disclosed in U.S. Patent No. 3,522,039 to McLain) or alloy C197 (0.3% - 1.6% iron, 0.01% - 0.20% magnesium, 0.10% - 0.40% phosphorous, up to 0.5% tin or antimony or mixtures thereof and the balance copper as disclosed in U.S. Patent No. 4,605,532 to Knorr et al.) to increase the dissipation of heat from the electronic device. The leadframe 20, the window frame 16 and the cover component 18 may be formed from a precipitation hardenable alloy to give the package 10 extra strength. Any desired combination of materials may be employed.

An example of a glass sealed metal package 10 in accordance with the present invention is illustrated in FIG. 1. A base component 14 is formed from a metal or metal alloy. Preferably, a high conductivity alloy such as copper alloy
C194 or C197 is utilized. A glass sealable layer 22 may be formed on at least a first surface 15 and, preferably, the edges of the base 14 as well.

The glass sealable layer is preferably a metal oxide or refractory oxide layer and may be applied by cladding. Other additive processes such as plating, sputtering or vapor deposition may also be used. If cladding is utilized, the clad is often several mils thick and may be removed from that portion of the base component 14 which will bond to the chip 12 to increase thermal conductivity. If plating, sputtering or vapor deposition is used, the coating is generally much thinner than a clad layer and it is usually not removed from the bonding site.

The glass sealable layer 22 is oxidized to form a refractory oxide 24 on the bonding surface. A sealing glass 26 having a composition in accordance with the present invention is applied to the refractory oxide by any applicable technique. One exemplary technique is to mix the glass powder with a suitable organic solvent such as mixing 10 parts of the glass with 1 part terpinol to form a paste. The paste is applied over a desired portion of the substrate by a technique such as screen printing. The paste is then glazed by heating in a furnace at a temperature of from about 600°C to about 750°C in air. Glazing evaporates the solvent from the paste. The glass particles stick to one another by sintering as well as to the oxide surface of the substrate.

After glazing, the parts may be handled
gently. Excessive handling may lead to bits of the loosely adherent glass flaking off.

A similar process provides a window frame 16 with a refractory oxide 28 on at least one surface. The window frame does not contribute significantly to thermal dissipation and is useful to increase the strength of the package. The window frame is preferably a precipitation hardened alloy. A glass 26 with a composition in accordance with the present invention is applied to the refractory oxide layer 28 of the window frame 16 and glazed.

The glazed base component 14 and the glazed window frame 16 are aligned with a leadframe 20 disposed between the two components. The leadframe is preferably formed from a precipitation hardenable alloy for strength, although a high conductivity copper alloy such as C194 or C197 may be used. To improve the glass to metal bond, it is often desirable to supply a refractory oxide layer to first 19 and second 21 sides of the leadframe 20.

The assembly is fired in a furnace at a temperature of about 750°C to about 850°C and, more preferably, at a temperature of from about 740°C to about 760°C for a time of about 5 minutes to about 15 minutes and, preferably, of about 5 minutes to about 10 minutes. The furnace atmosphere may be neutral or oxidizing, generally dependent on the composition of the package components. If the components are preoxidized, a neutral or reducing atmosphere, such as 4% H₂, 96% N₂ may be used. If the components are not preoxidized, a slightly oxidizing atmosphere, such as air or nitrogen
with a trace of water may be used.

After sealing, the package assembly contains a leadframe in the solutionized or soft state which is glass sealed to the base and to the window frame components. While the package is hermetic, the leadframe is subject to bending during handling. The glass is brittle and subject to moisture penetration. In accordance with this invention, the glass sealing system is capable of ceramization. The glass has been specifically designed to undergo ceramization at times and temperatures which age harden the preferred alloys.

The assembly is heated to a temperature of from about 550°C to about 750°C for a time of from about 15 minutes to about 90 minutes. A preferred profile for ceramization is to heat in the range of from about 620°C to about 650°C for a time of from about 30 minutes to about 60 minutes. A neutral atmosphere such as nitrogen is preferred during ceramization. During ceramization, both the glass and the leadframe undergo a transformation creating a superior electronic package. The nucleating agent precipitates a crystalline ceramic phase. The glass converts to a ceramic and a residual glass matrix. The glass-ceramic comprises from about 10% to about 60% a ceramic and the remainder a glass.

At the same time, the leadframe age hardens by aging. The resultant package has improved moisture penetration resistance due to the ceramization and improved resistance to leadframe distortion from age hardening.

Stresses are imparted in the glass-ceramic
during ceramization. The stresses are relieved by an optional, but preferred, post-ceramization anneal. The anneal takes place at temperatures of from about 350°C to about 450°C and most preferably at a temperature in the range of from about 390°C to about 420°C. A preferred time for annealing the glass is from about 15 minutes to about 30 minutes. While the glass is being annealed, the annealing cycle serves to further harden the leadframe.

Following ceramization, an electronic device 12 is bonded to the base component by any known die attach system 34. Suitable die attach systems include gold–silicon and lead–tin solders, conductive glasses as well as any other system known in the art. Since the coefficient of thermal expansion of the silicon device 12 is significantly less than the coefficient of thermal expansion of the base component 14, the use of a buffered die attach may be preferred. The buffer system incorporates a low coefficient of thermal expansion buffer, such as tungsten or molybdenum, positioned between the semiconductor device and the metal base component. The glass-ceramic does not deteriorate at die attach temperatures. This is a distinct advantage over conventional sealing glasses which may degrade at temperatures in excess of about 350°C. The electronic device 12 is then electrically connected to lead fingers 35 by a known process such as wire bonding 36.

A cover component 18 is attached to the second surface 40 of the window frame 16 by a suitable bonding component 38. The glass-ceramic is thermally stable at
temperatures of up to about 750°C, so the bonding component 38 is selected to have a melting temperature low enough to avoid damage to the electronic device and softening of the precipitation hardened copper alloys. It is preferable to select a bonding component which seals at temperatures less than about 400°C. Most conventional CERDIP bonding components, for example, low temperature solder glasses or alloys such as 80% by weight gold and 20% by weight tin or lead-tin alloys are acceptable.

The second surface 40 of the window frame and the cover component 18 are supplied with a refractory oxide if a solder glass is used as the bonding component 38. If a metallic bonding component is used, it is preferable to have the second surface 40 and cover component 18 bare metal or plated with a metal such as gold or tin to enhance solder wettability.

The package containing the window frame 16 and cover component 18 with a suitable bonding component 38 disposed therebetween is heated to seal the cover component to the package, thereby completing the hermetic package 10 in accordance with the present invention.

The present invention is not limited to hermetic metal packages as described above. The sealing glass may be used in combination with a metal or any metal alloy in any application where an approximate match in coefficients of thermal expansion is desired.

EXAMPLE 2

Referring to Figure 2, a composite 50 is shown in cross section. The composite is
comprised of a metal substrate 52 and a glass-ceramic layer 54. Optionally, a glass sealable layer 56 is disposed between the metal substrate and the glass-ceramic layer. The glass sealable layer may be a metal oxide or a refractory oxide as described hereinabove and may be applied by in situ or additive techniques.

The process of assembly is similar to that used for the electronic package. The glass is glazed to the substrate and then bonded by firing at the sealing temperature. After bonding, the glass is ceramicized to form the composite. An optional anneal reduces stresses developed within the composite.

The composite may be used to fabricate a circuit assembly such as a printed circuit board or a chip carrier. A circuit assembly is disclosed in U.S. Patent No. 4,491,622 to Butt. A conductive layer such as a metal foil layer 58 may be bonded to the glass as disclosed in U.S. Patent No. 4,712,161 to Pryor et al. Since the glass-ceramic has a coefficient of thermal expansion approximately equal to that of copper, a copper or copper alloy substrate may be used to take advantage of the high thermal conductivity of the copper. The increased strength and moisture penetration resistance of the glass-ceramic over conventional sealing glasses permits the manufacture of metal boards which are less prone to flexure glass fracture.

**EXAMPLE 3**

As shown in Figure 3, the glass-ceramic sealing system may be used to bond a plurality
of substrates in the manufacture of multi-layer circuits. A multi-layer circuit board 60 is comprised of first 62 and second 64 substrates. The substrates are any metal or metal alloy and, preferably, copper or a copper alloy. The sealing glass 66 is applied to at least one surface of each substrate as disclosed above and a conductive layer 68 such as copper foil 68 is added. It may be desirable to provide glass sealable layers 70 to the substrate and foil to facilitate glass sealing. The substrates are then stacked and bonded together.

The copper foil layers 68 are formed into circuit patterns, for example, by selectively applying a resist and then chemically etching away the uncovered portions of foil. Insulated conductive through-holes 72 may also be provided to supply electrical contact from one foil layer to the next.

Since the coefficient of thermal expansion of the glass, substrates and foil layers closely match, the multi-layer circuit is not limited to two layers as shown in Figure 3. Any number of substrates and foil layers may be used with through-hole supplying electrical interconnection. After the multi-layer board has been assembled, ceramization of the sealing glass significantly improves the strength and moisture resistance of the multi-layer circuit.

The glass-ceramic is also useful as a component in a decorative laminate. The glass limits oxidation and corrosion of the underlying substrate. Prior to ceramization, the glass is transparent and the underlying substrate is visible. Following ceramization, the
glass-ceramic is opaque white and may serve as a coloring enamel. Examples of decorative composite material formed from a metallic substrate and a glass layer may be found in U.S. Patent Nos. 3,826,627 and 3,826,629 both to Pryor et al. The laminate is useful for plumbing fixtures, bathroom fixtures or jewelry or other uses for an enameled metal. The coefficient of thermal expansion of a composite manufactured according to the present invention is close to that of copper or a copper alloy. Any application requiring enameled copper could preferably be made using the present glass and a copper or copper alloy substrate.

The advantages of a glass with a coefficient of thermal expansion which matches that of copper or a copper based alloy is not limited to electronic and decorative applications. Any matched seal between glass and a high expansion alloy is improved by the use of the glass of the present invention.

A useful application is matched glass to metal seals in vacuum devices. These devices may be used for electrical devices as disclosed in U.S. Patent No. 2,446,277 to Gordon or in pressurized vessels requiring glass to metal seals such as a chemical reaction chamber or even a submarine. The vessel need not be under vacuum, it may be pressurized or at atmospheric pressure.

It is apparent there has been provided in
accordance with this invention a glass-ceramic sealing system suitable for the assembly of hermetic metal packages. The packages so produced have improved strength and moisture penetration resistance. The glass-ceramic sealing system satisfies the objects, means and advantages set forth hereinabove. While the invention has been described in combination with the embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications and variations as fall within the spirit and broad scope of the appended claims.
IN THE CLAIMS:

1. A sealing glass capable of ceramization, characterized by said glass consisting essentially of:
   at least about 40 molar percent SiO₂;
   from about 5 molar percent to about 25 molar percent BaO;
   from about 15 molar percent to about 45 molar percent of an alkaline oxide component, said alkaline oxide component comprising at least two oxides selected from the group consisting of Li₂O, K₂O, Rb₂O₃ and Cs₂O₃;
   from about 0.1 molar percent to about 5 molar percent of a nucleating agent;
   up to about 15 molar percent ZnO;
   up to about 10 molar percent PbO;
   up to about 5 molar percent Al₂O₃; and
   up to about 10 molar percent of an additive.

2. The sealing glass of claim 1 characterized in that said additive is selected from the group consisting of B₂O₃, CaO, Ni₂O, TiO₂, SrO and combinations thereof.

3. The sealing glass of claim 2 characterized in that said nucleating agent is selected from the group consisting of V₂O₅ and P₂O₅.

4. The sealing glass of claim 3 characterized in that the concentration of said SiO₂ is from about 40 molar percent to about 50 molar percent.
5. The sealing glass of claim 4 characterized in that the concentration of said SiO₂ is from about 45 molar percent to about 48 molar percent.

6. The sealing glass of claim 3 characterized in that the concentration of said BaO component is from about 10 molar percent to about 20 molar percent.

7. The sealing glass of claim 6 characterized in that the concentration of said BaO component is from about 12 molar percent to about 15 molar percent.

8. The sealing glass of claim 3 characterized in that said alkaline oxide component consists of from about 5 molar percent to about 15 molar percent LiO₂ and from about 10 molar percent to about 30 molar percent K₂O.

9. The sealing glass of claim 8 characterized in that said LiO₂ concentration is from about 6 molar percent to about 9 molar percent.

10. The sealing glass of claim 8 characterized in that said K₂O concentration is from about 18 molar percent to about 22 molar percent.

11. The sealing glass of claim 3 characterized in that said V₂O₅ concentration is from about 0.3 molar percent to about 0.8 molar percent.
12. The sealing glass of claim 3 characterized in that said PbO concentration is less than about 6 molar percent.

13. The sealing glass of claim 12 characterized in that said PbO concentration is from about 4 molar percent to about 6 molar percent.

14. The sealing glass of claim 3 characterized in that said ZnO concentration is from about 6 molar percent to about 8 molar percent.

15. The sealing glass of claim 3 characterized in that said Al₂O₃ concentration is from about 1 molar percent to about 3 molar percent.

16. The sealing glass of claim 3 characterized by said glass consisting of:
   from about 45 molar percent to about 48 molar percent SiO₂;
   from about 12 molar percent to about 15 molar percent BaO;
   from about 6 molar percent to about 9 molar percent LiO₂;
   from about 18 molar percent to about 22 molar percent K₂O;
   from about 0.3 molar percent to about 0.8 molar percent V₂O₅;
   from about 4 molar percent to about 6 molar percent PbO;
   from about 6 molar percent to about 8 molar percent ZnO; and
   from about 1 molar percent to about 3 molar percent Al₂O₃.
17. A process of producing a sealing glass, characterized by the steps of:
   combining a desired molar ratio of the carbonates and oxides of silicon, barium, lithium, potassium, a nucleating agent and desired additives into a mixture;
   heating said mixture to a temperature in the range of from about 1300°C to about 1500°C;
   quenching said mixture;
   forming said glass into a form suitable for use as a sealing glass.

18. The process of claim 16 characterized in that said oxides are supplied in a molar ratio characterized by:
   from about 40 molar percent to about 50 molar percent SiO₂;
   from about 5 molar percent to about 25 molar percent BaO;
   from about 15 molar percent to about 45 molar percent of an alkaline oxide component, said alkaline oxide component comprising at least two oxides selected from the group consisting of Li₂O, K₂O, Rb₂O₃ and Cs₂O₃;
   from about 0.1 molar percent to about 5 molar percent of a nucleating agent;
   up to about 15 molar percent ZnO;
   up to about 10 molar percent PbO;
   up to about 5 molar percent Al₂O₃; and
   up to about 10 molar percent of an additive.

19. The process of claim 18 characterized in that said oxides are supplied in a molar ratio, consisting essentially of:
   from about 45 molar percent to about 48 molar percent SiO₂;
from about 12 molar percent to about 15 molar percent BaO;
from about 6 molar percent to about 9 molar percent Li₂O;
from about 18 molar percent to about 22 molar percent K₂O;
from about 0.3 molar percent to about 0.8 molar percent V₂O₅;
from about 4 molar percent to about 6 molar percent PbO;
from about 6 molar percent to about 8 molar percent ZnO; and
from about 1 molar percent to about 3 molar percent Al₂O₃.

20. The process of claim 19 characterized in that said mixture is heated to a temperature in the range of about 1325°C to about 1375°C.

21. The process of claim 17 characterized in that said glass is reduced to a powder having a size in the range of from about 15 microns to about 10 microns and combining said powder with a solvent.

22. The process of claim 21 characterized in that said solvent is terpinol.

23. A metal-glass/ceramic composite 50, characterized by:
a first metal or metal alloy substrate 52 and a glass/ceramic 54 bonded to said metal or metal alloy substrate 52.
24. The metal-glass/ceramic composite 50 of claim 23 characterized in that said glass/ceramic 54 consists essentially of:

5 percent SiO₂;

from about 5 molar percent to about 25 molar percent BaO;

from about 15 molar percent to about 45 molar percent of an alkaline oxide component, said alkaline oxide component comprising at least two oxides selected from the group consisting of Li₂O₂, K₂O, Rb₂O₃ and Cs₂O₃;

from about 0.1 molar percent to about 5 molar percent V₂O₅;

up to about 15 molar percent ZnO;

up to about 10 molar percent PbO;

up to about 5 molar percent Al₂O₃; and

up to about 10 molar percent of an additive.

25. The metal-glass/ceramic composite 50 of claim 24 characterized in that said glass/ceramic 54 wherein said glass/composite is characterized by:

5 percent SiO₂;

from about 12 molar percent to about 15 molar percent BaO;

from about 6 molar percent to about 9 molar percent Li₂O₂;

from about 18 molar percent to about 22 molar percent K₂O;

from about 0.3 molar percent to about 0.8 molar percent V₂O₅;

from about 4 molar percent to about 6 molar percent PbO;
from about 6 molar percent to about 8 molar percent ZnO; and
from about 1 molar percent to about 3 molar percent Al$_2$O$_3$.

26. The composite 50 of claim 24 characterized in that a glass sealable layer 56 is disposed between said metal substrate 52 and said glass ceramic 54.

27. The metal-glass/ceramic composite 50 of claim 26 characterized in that said glass sealable surface 56 of said metal or metal alloy substrate 52 comprises a refractory oxide.

28. The metal-glass/ceramic composite 50 of claim 24 characterized in that a conductive layer 58 having a desired circuit pattern is bonded to said composite 50.

29. The metal-glass/ceramic composite 60 of claim 28 characterized in that a plurality of conductive layers 68 having a plurality of desired circuit patterns are bonded to said metal or metal alloy substrate 62, 64, a layer of said glass/ceramic composite 66 disposed between each adjacent set of said conductive layers 68.

30. The metal-glass/ceramic composite 60 of claim 29 characterized in that said conductive layer 68 comprises copper or copper foil formed into a desired circuit pattern.
31. A process of forming a composite material characterized by the steps of:
applying a ceramizable sealing glass to a metal or metal alloy substrate;
glazing said sealing glass to said metal or metal alloy substrate;
bonding said sealing glass to said metal or metal alloy substrate.

32. The process of claim 31 characterized in that said ceramizable sealing glass is selected to have a composition characterized by:
from about 40 molar percent to about 50 molar percent SiO₂;
from about 5 molar percent to about 25 molar percent BaO;
from about 15 molar percent to about 45 molar percent of an alkaline oxide component, said alkaline oxide component comprising at least two oxides selected from the group consisting of LiO₂, K₂O, Rb₂O₃ and Cs₂O₃;
from about 0.1 molar percent to about 5 molar percent V₂O₅;
up to about 15 molar percent ZnO;
up to about 10 molar percent PbO;
up to about 5 molar percent Al₂O₃; and
up to about 10 molar percent of an additive.

33. The process of claim 32 characterized in that said sealing glass is selected to have a composition characterized by:
from about 45 molar percent to about 48 molar percent SiO₂;
from about 12 molar percent to about 15 molar percent BaO;
from about 6 molar percent to about 9 molar percent LiO₂;

from about 18 molar percent to about 22 molar percent K₂O;

from about 0.3 molar percent to about 0.8 molar percent V₂O₅;

from about 4 molar percent to about 6 molar percent PbO;

from about 6 molar percent to about 8 molar percent ZnO; and

from about 1 molar percent to about 3 molar percent Al₂O₃.

34. The process of claim 32 characterized in that said glass 54 is glazed to said metal or metal alloy substrate 52 at a temperature of from about 600°C to about 750°C.

35. The process of claim 34 characterized in that said glass 54 is bonded to said metal or metal alloy substrate 52 at a temperature of from about 750°C to about 850°C.

36. The process of claim 35 characterized in that said glass 54 is bonded to said metal or metal alloy substrate 52 at a temperature of from about 740°C to about 760°C.

37. The process of claim 35 characterized in that said glass 54 is bonded to said metal or metal alloy substrate 52 in a neutral to oxidizing atmosphere.
38. The process of claim 35 characterized by forming a refractory oxide layer 24 on the surface 56 of said metal or metal alloy substrate 52 prior to glazing said sealing glass 54.

39. The process of claim 38 characterized in that said refractory oxide layer 24 is formed in situ.

40. The process of claim 38 characterized by forming a refractory oxide layer 24 on the surface 56 of said metal or metal alloy substrate 52 by an additive process.

41. The process of claim 35 characterized by the step of ceramization of said sealing glass 54 subsequent to said bonding step.

42. The process of claim 41 characterized in that said composite 50 is heated to a temperature of from about 550°C to about 750°C to ceramize said sealing glass 54.

43. The process of claim 42 characterized by ceramizing said sealing glass 54 in nitrogen.

44. The process of claim 42 characterized in that said composite 50 is annealed subsequent to said ceramization step.

45. The process of claim 42 characterized in that said composite 50 is annealed to a temperature of from about 390°C to about 420°C.
46. A package 10 adapted to house an electronic device 12, characterized by:
   a metal or metal alloy base component 14;
   a metal or metal alloy window frame component 16;
   a leadframe 20 disposed between said base component 14 and said window frame component 16;
   a glass/ceramic sealing system 26 to bond said leadframe 20 to said base component 14 and to said window frame component 16;
   a cover component 18; and
   a means 38 for bonding said cover component 18 to said window frame component 16.

47. The package 10 of claim 46 characterized in that said base component 14, window frame component 16 and leadframe 20 are copper or a copper based alloy.

48. The package 10 of claim 47 characterized in that said leadframe 20 is a precipitation hardened copper alloy and said base component 14 is copper or a dilute copper alloy.

49. The package 10 of claim 48 characterized in that said leadframe 20 is selected from the group consisting of copper alloy 725 and copper alloy 7025.

50. The package 10 of claim 49 characterized in that said base component 14 is selected from the group consisting of OFHC copper, copper alloy 194, copper alloy 197 and copper alloy 638.
51. The package 10 of claim 50 characterized in that said means 38 for sealing said cover component 18 to said window frame component 16 is selected from the group consisting of solder glasses, metal solders and polymer adhesives.

52. The package 10 of claim 48 characterized in that said glass/ceramic sealing system 26 has a composition characterized by:

- from about 40 molar percent to about 50 molar percent SiO$_2$;
- from about 5 molar percent to about 25 molar percent BaO;
- from about 15 molar percent to about 45 molar percent of an alkaline oxide component, said alkaline oxide component comprising at least two oxides selected from the group consisting of LiO$_2$, K$_2$O, Rb$_2$O$_3$ and Cs$_2$O$_3$;
- from about 0.1 molar percent to about 5 molar percent V$_2$O$_5$;
- up to about 15 molar percent ZnO;
- up to about 10 molar percent PbO;
- up to about 5 molar percent Al$_2$O$_3$; and
- up to about 10 molar percent of an additive.

53. The package 10 of claim 52 characterized in that said glass/ceramic sealing system 26 consists essentially of:

- from about 45 molar percent to about 48 molar percent SiO$_2$;
- from about 12 molar percent to about 15 molar percent BaO;
- from about 6 molar percent to about 9 molar percent LiO$_2$;
from about 18 molar percent to about 22 molar percent $K_2O$;
from about 0.3 molar percent to about 0.8 molar percent $V_2O_5$;
from about 4 molar percent to about 6 molar percent $PbO$;
from about 6 molar percent to about 8 molar percent $ZnO$; and
from about 1 molar percent to about 3 molar percent $Al_2O_3$.

54. A process for assembling a package 10 adapted to house an electronic package 12, characterized by:
providing a base component 14;
providing a window frame component 16;
disposing a leadframe 20 between said base component 14 and said window frame component 16;
bonding said leadframe 20 to said base component 14 and to a first side 28 of said window frame 16 with a ceramizable 18 sealing glass 26;
bonding a cover component to a second side of said window frame 40 thereby sealing said package 10.

55. The process of claim 54 characterized in that said ceramizable sealing glass 26 is selected to have a composition consisting essentially of:
from about 40 molar percent to about 50 molar percent $SiO_2$;
from about 5 molar percent to about 25 molar percent $BaO$;
from about 15 molar percent to about 45 molar percent of an alkaline oxide component, said alkaline oxide component comprising at least two oxides selected from the group consisting of LiO₂, K₂O, Rb₂O₃ and Cs₂O₃;
from about 0.1 molar percent to about 5 molar percent V₂O₅;
up to about 15 molar percent ZnO;
up to about 10 molar percent PbO;
up to about 5 molar percent Al₂O₃; and
up to about 10 molar percent of an additive.

56. The process of claim 54 characterized by forming said base component 14, said window frame 16 and said leadframe 20 from copper or a copper base alloy.

57. The process of claim 56 characterized in that said leadframe 20 is formed from a precipitation hardenable copper alloy.

58. The process of claim 57 characterized in that said leadframe 20 is formed from a precipitation hardenable copper alloy selected from the group consisting of copper alloy 724 and copper alloy 7025.

59. The process of claim 56 characterized by forming said base component 14 from copper or a dilute copper alloy.

60. The process of claim 59 characterized in that said base component 14 is formed from copper or a copper alloy selected from the group consisting of copper alloy 194, copper alloy 197 and copper alloy 638.
61. The process of claim 59 characterized by glazing said glass 26 to said base component 14 and said window frame component 16 prior to bonding said leadframe 20.

62. The process of claim 61 characterized by glazing at a temperature of from about 600°C to about 750°C.

63. The process of claim 62 characterized by forming a refractory oxide 28 on the surface 22, 28 of said base component 14 and said window frame component 16 prior to said glazing step.

64. The process of claim 63 characterized in that said glass 26 is bonded to said leadframe 20 at a temperature sufficient to bond said glass and to solutionize said precipitation hardenable copper leadframe 20.

65. The process of claim 64 characterized in that said glass 26 is bonded at a temperature in the range of from about 780°C to about 850°C for a time of from about 5 minutes to about 15 minutes.

66. The process of claim 65 characterized by the bending the lead ends 30 of said leadframe 20 to a desired radius 32 while said leadframe 20 is in the solutionized state.

67. The process of claim 66 characterized by ceramizing said sealing glass 26 subsequent to bonding and simultaneously age hardening said leadframe 20.
68. The process of claim 67 characterized by ceramizing said glass 26 at a temperature of from about 550°C to about 750°C for a time of from about 15 minutes to about 90 minutes.

69. The process of claim 68 characterized in that said glass/ceramic 26 is annealed subsequent to said ceramization step.

70. The process of claim 69 characterized by annealing at a temperature of from about 390°C to about 420°C for a time of from about 15 minutes to about 30 minutes.
1. A sealing glass capable of ceramization, characterized by said glass having a coefficient of thermal expansion of from about 160 x 10^{-7} \text{cm/cm/°C} to about 180 x 10^{-7} \text{cm/cm/°C} and consisting essentially of:

- from about 40 to about 50 molar percent SiO_2;
- from about 5 to about 25 molar percent BaO;
- from about 15 to about 45 molar percent of an alkaline oxide component, said alkaline oxide component consisting of at least two oxides selected from the group consisting of LiO_2, K_2O, Rb_2O_3 and Cs_2O_3;
- from about 0.1 to about 5 molar percent of a nucleating agent selected from the group consisting of V_2O_5 and P_2O_5;
- up to about 15 molar percent ZnO;
- up to about 10 molar percent PbO;
- up to about 5 molar percent Al_2O_3; and
- up to about 10 molar percent of an additive selected from the group consisting of B_2O_3, CaO, Ni_2O, TiO_2, SrO and combinations thereof.
17. A process of producing a ceramicizable sealing glass having a coefficient of thermal expansion from about $160 \times 10^{-7}$ cm/cm/°C to about $180 \times 10^{-7}$ cm/cm.°C, characterized by the steps of:

- combining a mixture consisting essentially of from about 40 to about 50 molar percent SiO$_2$, from about 5 to about 25 molar percent BaO, from about 15 molar percent to about 45 molar percent of an alkaline oxide component consisting of at least two oxides selected from the group consisting of LiO$_2$, K$_2$O, Rb$_2$O$_3$ and Cs$_2$O$_3$, from about 0.1 to about 5 molar percent for a nucleating agent selected from the group consisting of V$_2$O$_5$ and P$_2$O$_5$, up to about 15 molar percent ZnO, up to about 10 molar percent PbO, up to about 5 molar percent Al$_2$O$_3$ and up to about 10 molar percent of an additive selected from the group consisting of B$_2$O$_3$, CaO, Ni$_2$O, TiO$_2$, SrO and combinations thereof;
- heating said mixture to a temperature in the range of from about 1300°C to about 1500°C;
- quenching said mixture;
- forming said glass into a form suitable for use as a sealing glass 26.

19. The process of claim 17 characterized in that said oxides are supplied in a molar ratio consisting essentially of:

- from about 45 molar percent to about 48 molar percent SiO$_2$;
from about 12 molar percent to about 15 molar percent BaO;
from about 6 molar percent to about 9 molar percent LiO₂;
from about 18 molar percent to about 22 molar percent K₂O;
from about 0.3 molar percent to about 0.8 molar percent V₂O₅;
from about 4 molar percent to about 6 molar percent PbO;
from about 6 molar percent to about 8 molar percent ZnO; and
from about 1 molar percent to about 3 molar percent Al₂O₃.

20. The process of claim 19 characterized in that said mixture is heated to a temperature in the range of about 1325°C to about 1375°C.

21. The process of claim 17 characterized in that said glass is reduced to a powder having a size in the range of from about 5 microns to about 10 microns and combining said powder with a solvent.

22. The process of claim 21 characterized in that said solvent is terpinol.

23. A metal-glass/ceramic composite 50, characterized by;
a first metal or metal alloy substrate 52 and
a glass/ceramic 54 having a coefficient of thermal expansion of from about 160 x 10⁻⁷ cm/cm/°C to about 180 x 10⁻⁷ cm/cm/°C bonded to said metal or metal alloy substrate 52.
31. A process of forming a composite material characterized by the steps of:
   applying a ceramizable sealing glass having a coefficient of thermal expansion of from about
   $160 \times 10^{-7}$ cm/cm/$^\circ$C to about $180 \times 10^{-7}$ cm/cm/$^\circ$C to
   a metal or metal alloy substrate;
   glazing said ceramizable sealing glass to said metal or metal alloy substrate;
   bonding said ceramizable sealing glass to said metal or metal alloy substrate.

32. The process of claim 31 characterized in that said ceramizable sealing glass is selected to have a composition characterized by:
   from about 40 molar percent to about 50 molar percent $\text{SiO}_2$;
   from about 5 molar percent to about 25 molar percent $\text{BaO}$;
   from about 15 molar percent to about 45 molar percent of an alkaline oxide component, said alkaline oxide component comprising at least two oxides selected from the group consisting of $\text{Li}_2\text{O}$, $\text{K}_2\text{O}$, $\text{Rb}_2\text{O}_3$ and $\text{Cs}_2\text{O}_3$;
   from about 0.1 molar percent to about 5 molar percent $\text{V}_2\text{O}_5$;
   up to about 15 molar percent $\text{ZnO}$;
   up to about 10 molar percent $\text{PbO}$;
   up to about 5 molar percent $\text{Al}_2\text{O}_3$; and
   up to about 10 molar percent of an additive.

33. The process of claim 32 characterized in that said sealing glass is selected to have a composition characterized by:
   from about 45 molar percent to about 48 molar percent $\text{SiO}_2$;
   from about 12 molar percent to about 15 molar percent $\text{BaO}$;
46. A package 10 adapted to house electronic device 12, characterized by:
   a metal or metal alloy base component 14;
   a metal or metal alloy window frame component 16;
   a leadframe 20 disposed between said base component 14 and said window frame component 16;
   a glass/ceramic sealing system 26 having a coefficient of thermal expansion of from about $160 \times 10^{-7}$ cm/cm/°C to about $180 \times 10^{-7}$ cm/cm/°C to bond said leadframe 20 to said base component 14 and to said window frame component 16;
   a cover component 18; and
   a means 38 for bonding said cover component 18 to said window frame component 16.

47. The package 10 of claim 46 characterized in that said base component 14, window frame component 16 and leadframe 20 are copper or a copper based alloy.

48. The package 10 of claim 47 characterized in that said leadframe 20 is a precipitation hardened copper alloy and said base component 14 is copper or a dilute copper alloy.

49. The package 10 of claim 48 characterized in that said leadframe 20 is selected from the group consisting of copper alloy 724 and copper alloy 7025.

50. The package 10 of claim 49 characterized in that said base component 14 is selected from the group consisting of OFHC copper, copper alloy 194, copper alloy 197 and copper alloy 638.
from about 18 molar percent to about 22 molar percent $K^2O$;
from about 0.3 molar percent to about 0.8 molar percent $V_2O_5$;
from about 4 molar percent to about 6 molar percent $PbO$;
from about 6 molar percent to about 8 molar percent $ZnO$; and
from about 1 molar percent to about 3 molar percent $Al_2O_3$.

54. A process for assembling a package 10 adapted to house an electronic package 12, characterized by:
   providing a base component 14;
   providing a window frame component 16;
   disposing a leadframe 20 between said base component 14 and said window frame component 16;
   bonding said leadframe 20 to said base component 14 and to a first side 28 of said window frame component 16 with a ceramizable 18 sealing glass having a coefficient of thermal expansion of from about $160 \times 10^{-7} \text{cm/cm/°C}$ to about $180 \times 10^{-7} \text{cm/cm/°C}$;
   bonding a cover component to a second side 40 of said window frame 16 thereby sealing said package 10.

55. The process of claim 54 characterized in that said ceramizable sealing glass 26 is selected to have a composition consisting essentially of:
   from about 40 molar percent to about 50 molar percent $SiO_2$;
   from about 5 molar to about 25 molar percent $BaO$;
In response to the International Search Report mailed 06 December 1989, Applicant has submitted replacement pages 27, 30, 31, 34, 37 and 39 in the above referenced International Application. As a result of the amendment, claims 1, 17, 21, 23, 31, 46, 49 and 54 have been amended. Claims 2, 3, 4, 18 have been cancelled. Applicant believes that claim 1 as amended more clearly identifies the invention and the novelty of the pending claims.

With reference to Applicant's claim 1 as amended, the alkaline oxide component consists of at least two oxides selected from the group consisting of LiO₂, K₂O, Rb₂O₃ and Cs₂O₃. The limited transition phrase "consisting" indicates that Applicant's alkaline oxide component excludes those not included within the group.

Na₂O is excluded. The Stookey ('941) reference discloses glasses containing either a single alkaline oxide or a mixture of Na₂O and K₂O. There is nothing to teach or suggest a mixture of alkaline oxides excluding Na₂O.

Support for this amendment may be found in Applicant's specification at page 9, lines 5-10 where the preferred alkaline oxides are stated and sodium oxide is specified as not preferred.
The preamble to claim 1 has been amended to indicate that the ceramizable sealing glass has a coefficient of thermal expansion in the range of $160 \times 10^{-7}$ to $180 \times 10^{-7}$ cm/cm/°C. This coefficient of thermal expansion is novel in view of the Oldfield reference which specifies a coefficient of thermal expansion of $145-155 \times 10^{-7}$ cm/cm/°C and the Omori reference which discloses glasses with coefficients of thermal expansion of from $100-102 \times 10^{-7}$ cm/cm/°C. The Omori glasses further include sodium oxide. Support for Applicants' insertion of a coefficient of thermal expansion range may be found in Applicants' specification at page 8, lines 2-7.

Applicant's claim 1 as amended further limits the concentration of silicon dioxide to from about 40 to about 50 molar percent. This limitation was accomplished by incorporating Applicant's claim 4 into claim 1. The silicon dioxide concentration of claim 1 is now outside the range disclosed in the Stookey (‘803) reference.

Claim 1 as amended claims the nucleating agent is $V_2O_5$ or $P_2O_5$. Neither nucleating agent is disclosed in the Robertson reference.

Entry of the replacement pages and reconsideration of the claims in view of the enclosed amendment and above remarks is respectfully solicited.
INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to joint National Classification and IPC:

IPC (4) C03C 3/078, 8/02, 10/04; B32B 15/06; B44C 1/22
U.S. CL 65/134; 156/663; 428/433; 501/5,21,72

II. FIELDS SEARCHED

<table>
<thead>
<tr>
<th>Classification System</th>
<th>Classification Symbols</th>
</tr>
</thead>
<tbody>
<tr>
<td>US</td>
<td>65/134; 156/663; 428/433; 501/5,21,60,61,62,63,65,66,67,69,72</td>
</tr>
</tbody>
</table>

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X Y</td>
<td>US, A, 2,515,941 (STOOKEY), 18 JULY 1950 SEE ENTIRE DOCUMENT</td>
<td>1-16</td>
</tr>
<tr>
<td>X Y</td>
<td>US, A, 2,948,992 (OLDFIELD ET AL.), 16 AUGUST 1960 SEE ENTIRE DOCUMENT</td>
<td>1-16</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 3,473,999 (MUCHTON), 21 OCTOBER 1969 SEE ENTIRE DOCUMENT</td>
<td>23-70</td>
</tr>
<tr>
<td>X Y</td>
<td>US, A, 3,498,803 (STOOKEY), 03 MARCH 1970 SEE ENTIRE DOCUMENT</td>
<td>1-16</td>
</tr>
<tr>
<td>X Y</td>
<td>US, A, 3,808,154 (OMORI), 30 APRIL 1974 SEE ENTIRE DOCUMENT</td>
<td>1-16</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 3,826,627 (PRYOR ET AL.), 30 JULY 1974 SEE ENTIRE DOCUMENT</td>
<td>23-70</td>
</tr>
<tr>
<td>Y</td>
<td>US, A, 3,826,629 (PRYOR ET AL.), 30 JULY 1974 SEE ENTIRE DOCUMENT</td>
<td>23-70</td>
</tr>
<tr>
<td>X Y</td>
<td>US, A, 3,939,295 (ROBERTSON ET AL.), 17 FEBRUARY 1976 SEE ENTIRE DOCUMENT</td>
<td>1-16</td>
</tr>
</tbody>
</table>

* Special category of cited documents:
  - "X" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  - "E" earlier document but published on or after the international filing date
  - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
  - "O" document referring to an oral disclosure, use, exhibition or other means
  - "P" document published prior to the international filing date but later than the priority date claimed

IV. CERTIFICATION

Date of the Actual Completion of the International Search: 27 NOVEMBER 1989
Date of Mailing of this International Search Report: 06 DEC 1989

International Searching Authority: ISA/US
Signature of Authorized Officer: Mark Bell
### FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

| Y | US, A, 4,491,622 (BUTT), 01 JANUARY 1985 | 23-70 |
| Y | US, A, 4,524,238 (BUTT), 18 JUNE 1985 | 23-70 |
| Y | US, A, 4,656,499 (BUTT), 07 APRIL 1987 | 23-70 |
| Y | US, A, 4,704,626 (BUTT), 03 NOVEMBER 1987 | 17-70 |

### V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. **Claim numbers**, because they relate to subject matter not required to be searched by this Authority, namely:

   - [Blank]

2. **Claim numbers**, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

   - [Blank]

3. **Claim numbers**, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

### VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This international searching Authority found multiple inventions in this international application as follows:

1. **Sealing Glass**: Claims 1-16, classifiable in Cl. 501/5.
2. **Process of Producing a Sealing Glass**: Claims 17-22, classifiable in Cl. 65/134.

   - [Blank] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

   - [Blank] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

   - [Blank]

   - [Blank] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

   - [Blank]

   - [Blank] As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

**Remark on Protest**

- [Blank] The additional search fees were accompanied by applicant's protest.
- [Blank] No protest accompanied the payment of additional search fees.
Continued from Paragraph VI.

classifiable in class 428/433.

IV. Process of forming a composite: Claims 31-45 and 54-70, classifiable in class 156/663.