Experiment on heat treatment of glass ceramics, i.e. crystallization

Objective: to demonstrate the process of crystallization from an amorphous matrix in a ceramic system of commercial and technological significance.

The aim of this experiment is to illustrate the importance of phase transformations and their impact on properties by studying the process of crystallization in glass ceramics. Glass ceramics are an interesting class of materials that have been developed fairly recently. They have a wide range of applications from cookware to glass-to-metal seals. The latter application is of interest here: metals have large thermal expansion coefficients (CTEs) whereas insulators typically have rather low CTEs. In order to make an insulator-to-metal seal, an insulator with an unusually high CTE must be made. The particular glass ceramic that we will work with, donated by Schott Glass is just such a material. It was developed at the Sandia National Laboratories in the 1960s and 1970s and a patent in that series is reproduced below. It is based on the Li$_2$O-ZnO-SiO$_2$ system but with additions of P$_2$O$_5$, Al$_2$O$_3$, B$_2$O$_3$ and K$_2$O. The composition is in the range SiO$_2$ (65-80%), Li$_2$O (8-16%), Al$_2$O$_3$ (2-8%), K$_2$O (1-8%), P$_2$O$_5$ (1-5%), B$_2$O$_3$ (0.5-7%), and ZnO (0-5%). The presence of the phosphorus oxide is known is to increase nucleation densities: without this addition, glass ceramics typically have too-coarse microstructures for practical use.

Background: see section 5.6 from Physical Ceramics (p. 430 et seq.)

[From lecture notes for 27-322]
Glasses are not simply "frozen liquids." If one examines the variation of molar volume with temperature for typical glass forming compositions, there is a temperature (the glass transition temperature, $T_g$) that is characteristic of the cooling rate at which there is a discontinuity in slope. Above $T_g$ the slope is characteristic of a liquid but below this the slope is solid-like. If crystallization occurs, there is (almost always) a change in molar volume in addition to the change in slope. For practical purposes, three temperatures are defined that are related to the formal glass transition temperature: the working point is the temperature at which the viscosity ($\eta$)=10$^4$; the softening point corresponds to $\eta$=10$^{7.6}$; the annealing point is that temperature at which internal stresses can be relieved in 15 minutes or less, $\eta$=10$^{13.4}$. The viscosity at the glass transition temperature is in the range $\eta$=10$^{13.4}$-14.5.

Although radius ratios are an excellent guide to the stability of ionic structures and other crystal structures, the conditions under which glasses are stable require additional criteria.
Zachariasen formulated a set of rules that are analogous to Pauling's rules for crystal structure stability. They are follows.

1) Each oxygen atom is linked to no more than two cations.
2) The number of oxygen atoms surrounding the cation must be small, i.e. 4 or less.
3) The oxygen polyhedra share corners rather edges of faces.
4) At least three corners of each oxygen polyhedra are shared.

These rules are quite useful for explaining the network forming capability of oxides such as $\text{B}_2\text{O}_3$, $\text{GeO}_2$, $\text{P}_2\text{O}_5$, and of course $\text{SiO}_2$. The discussion on the effect of network modifiers such as the alkali metals is given above. The replacement of a covalent bond between Si and O by an ionized oxygen and the cation (Na, K etc.) is the crucial structural change that shortens the effective average chain length. Oddly, in the borate glasses, the charge redistribution that occurs with alkali additions allows $\text{BO}_4$ units to participate on network formation, thereby increasing average network lengths. This effect explains the apparent boron anomaly, and the minimum in thermal expansion coefficient that occurs as alkalis are added to a borate glass [see fig. 1.51 in Physical Ceramics].

Materials processing texts rarely discuss glass processing and specialized texts must be consulted. The early stages of glass processing are mostly concerned with melting the components of glass (high quality silica sands, soda ash, modifying oxides), ensuring adequate mixing in what are often relatively viscous melts (compared with metals), and removing product on a continuous or semi-continuous basis. Recycled glass is useful in order to provide a low melting point material (the cullet) that then dissolves the solid oxides in the feedstock (silica, alumina, soda ash). Gas fired reverberatory furnaces are typical, although electrical heating is also very useful, especially if it is important to avoid contamination. Mixing is a significant challenge and additives such as sulphate powders are used (“fining”) to provide large volumes of gas bubbles which provide a strong stirring action. Refractories are very important to glass melting furnaces: high temperature oxides such as zirconia-alumina-silica mixtures are used. For very high purity systems, platinum crucibles are used, e.g. glass fibers.

As with steels, large volumes of glass are sold for windows as flat sheet. In recent years, the technology has come to be dominated by the float glass process in which the liquid glass is allowed to float on a bath of liquid metal (e.g. tin). The liquid metal substrate allows the glass to solidify (in the specialized sense applicable to amorphous materials) while maintaining an extremely flat surface. This avoids the very expensive post-solidification grinding and polishing traditionally required for plate glass. Older methods of making plate glass (e.g. for windows) produced a much less uniform product. Post-forming treatment is useful also: annealing out residual stresses is sometimes necessary. Also, thermal tempering is very important for developing desirable patterns of thermal stress; e.g. rapid heating and then cooling of the surface produces compressive stresses near the surface (and tensile inside), which resist crack propagation in the glass from surface flaws.
Glass formation in silica based systems depends on the arrangement of silica tetrahedra and added components. The lithia-ZnO-silica system offers a considerable range of composition over which glass formation is possible. The following diagram from McMillan illustrates this point: note that the compositions on the diagram are in mole % whereas the data in the patent (appendix) are in weight %. You may find it instructive to convert the composition(s) in the appendix to mole % and compare to the region of glass formation in the diagram.

1) **Annealing Treatments** to first nucleate then grow the crystalline phase(s)

This is standard for glass ceramics, i.e. to nucleate a high density of crystals at a low temperature, say 500°C, and then grow them at a higher temperature, say 650°C. The following figure from McMillan shows a typical microstructure that results from a
nucleation treatment (550°C, 1 hr). The precipitate is most likely lithium silicate although no (crystalline) diffraction pattern could be obtained from the specimen.

These treatments will take some time, so it will be important to have multiple ovens available at different temperatures. Some students may be required to come in early in order to perform the nucleation treatments. We will have to pay attention to the way in which specimens are transferred from one furnace to another in order to avoid letting them cool too quickly. Also, care will be needed to not cool specimens too quickly once their annealing period is complete, i.e. furnace cooling may be necessary.

The following diagram is taken from *Physical Ceramics* to illustrate a typical processing sequence for glass ceramics.

**Fig. 5.75** Typical processing cycle for Li$_2$O-Al$_2$O$_3$-SiO$_2$ glass ceramics.

Suggested heat treatments:
500°C, 1 hour (no visible change, but nucleation has occurred)
Set 1:
500°C, 1 h + 675°C, 1h
500°C, 1 h + 675°C, 2h
500°C, 1 h + 675°C, 4h
500°C, 1 h + 675°C, 8h (maybe longer for overnight convenience)
500°C, 1h +
Set 2:
500°C, 1 h + 700°C, 15m
500°C, 1 h + 700°C, 30m
500°C, 1 h + 700°C, 1h
500°C, 1 h + 700°C, 8h
Set 3:
500°C, 1 h + 725°C, 15 mins.
500°C, 1 h + 725°C, 30 mins.
500°C, 1 h + 725°C, 1h
500°C, 1 h + 725°C, 2h
850°C, 8h  (for coarse microstructure lacking nucleation step)

Note that last year (2001) growth treatments at 650, 750 and 850 °C were used. It turned out that 650°C was too low and yielded very slow growth. 750 and 850°C resulted in transformation that was too rapid to be effectively measured over the course of a few hours. As a result, a narrower band of temperatures has been chosen for this year.

Recommended procedure:
If you are performing only one heat treatment, then you only need to have one furnaces available: it is critical, however, to make sure that it has been at the specified temperature for at least an hour before you use it, so that its temperature is reasonably stable and uniform. If necessary, negotiate with Mr. Tom Gambal to have the furnace turned on the previous evening. If you want to perform multiple heat treatments (i.e. isothermal anneals for different times, at the same temperature) you must have two furnaces available, one at the required temperature and one at a lower temperature, say at 500°C. The lower temperature furnace will serve as a location to stage the cool-down since it is important to not cool the specimens too rapidly! Place the samples to be treated in the furnace and leave them there for the prescribed length of time. When their time is completed, either turn the furnace off (single time) and leave them in to furnace cool, or transfer them to the lower temperature furnace, wait for 30 minutes and then turn off the lower temperature furnace. If the latter is at 500°C, then it is acceptable to accumulate specimens in that furnace during the day and only turn it off at the end of the day.

The first treatment will show little visible effect but we may be able to detect the appearance of a crystalline phase in X-ray. The next 4 will develop crystallinity to various degrees. The last treatment should illustrate a coarse grain structure from omitting the nucleation step.

Some students may have to be given pre-treated specimens in order to start on the characterization, below.
2) **Characterization** of the partially crystallized materials.

We will aim to show how various properties of the material change as a function of crystallization. The most important techniques will be Vickers diamond pyramid micro-hardness testing (for hardness and fracture toughness) and x-ray diffraction.

**X-ray diffraction** will be performed to ascertain which crystalline phases appear. With some care (and approximations) we may be able to extract a fraction transformed and analyze the results according to the JMAK relationship. Expected results include the identification of crystalline phases such as lithium silicate and cristobalite (a form of quartz). Based on the trial experiments carried out to date, heat treatments below 700°C will result in the appearance of lithium silicate only. Heat treatments above 700°C will result in an additional crystalline phase. Document the scans obtained and identify as many of the diffraction peaks as you can. Also, the fraction crystallized will be extracted from the intensities of the peaks (seek guidance from Jason Wolf). It may not be possible to observe peaks from crystalline material until late in the process, i.e. longer annealing times. You will be using the new Phillips diffractometer which offers the advantage of highly automated software for analysis of powder (Debye-Scherrer) patterns.

**Hardness** will be performed with the Vickers microhardness tester. You may need to experiment with the load in order to obtain indents of a measurable size but not have gross cracking occur. In 2001, some groups used a load of 500 gm, and some used a load of 1,000 gm (the maximum). This will be somewhat time consuming and there is only one instrument so the following approach is required. Each student in a group will take one (or two) specimens and be responsible for them. You should take a specimen and use the Vickers instrument to apply at least 4 indents in a definite pattern. In 2001, we used a scribe to make a line on the surface and then placed a series of indents in a line next to the scribed line. Then take the specimen to the microscopes and measure the indent size and crack lengths. Be sure to check the calibration (i.e. magnifications) of the microscopes by taking images of a graduated scale of reticle (available from Mr. Tom Gambal). The hardness can be calculated from the load, $P$, and the size of the indent (measure diagonally across the points of the square shaped indent, i.e. the maximum linear dimension) as $H=1.72 \frac{P}{d^2}$. In order to obtain a result in, say, MPa, be sure to convert the load from weight to force by multiplying by 9.8 m.s\(^{-2}\) (i.e. gravitational acceleration) and the appropriate power of ten. In 2001, the hardness was found to vary little with annealing treatment.
Fracture Toughness will be measured by observing radial cracks emanating from the indents, based on the analysis given in the handout from Green's book on the mechanical properties of ceramics. Expected results include observations of hardness increasing with transformation, though not by a large amount. In order to reach any conclusions about the variation (or lack thereof) in hardness, you will have to make multiple measurements on the same specimen.

Note that the fracture toughness is expected to increase from very low values typical of glasses (less than 1 MPa√m) to values corresponding to brittle ceramics (<5 MPa√m). This part of the experiment is somewhat novel in that I am not aware of any specific experiments to investigate the variation in toughness as a function of heat treatment in this class of material. Use the following formula for calculating the toughness, \( K_c \):

\[
K_c = \sqrt{E/H} \cdot \left( \frac{P}{c_0^{3/2}} \right)
\]

where \( d = 0.016 \) (and has been determined from calibration tests), \( E \) is Young’s modulus (in GPa), \( H \) is the Vickers hardness (also in GPa: make sure that \( E \) and \( H \) are in the same units), \( P \) is the indentation load (in MN) and \( c_0 \) is the crack length (in meters, center of indent to end of crack – average the four lengths for each crack). Provided that \( P \) is given in mega-newtons and \( c \) is in meters, then the toughness will be in units of MPa√m. Since we are not measuring Young’s modulus independently, use the value mentioned below, \( E = 54 \text{GPa} \). In 2001, the toughness was found to increase slightly with annealing time.

Microstructure will be performed by optical microscopy, if time is available. Obviously the expected results are that grain structure will only be observable for the higher temperatures and longer times. Macmillan's book notes that etching with HF helps to reveal grain structure, especially for examination in the SEM. The latter might be a possibility, especially if a means of coating the specimens can be identified. The following figure from McMillan's book shows how the grain size and morphology varies in a phosphorus containing glass exposed to different nucleation treatments. You should concentrate on the highest temperature treatments as the first priority for microstructure characterization because they will have the coarsest structures.
Optical opacity will also be measured in a simple fashion using photometers. This will provide limited information on the progress of the crystallization. By identifying the phases and their spacing(s), however, it may be possible to apply some elementary optical theory against which our results can be compared. Record the light intensity both with and without your glass-ceramic specimen in the light path. What you should observe is a gradual loss of transparency as the material crystallizes. The parameter of interest is the fractional change in absorption, i.e. the measured change in light intensity divided by the maximum change observed. The uncrystallized glass is essentially fully
transparent (no absorption of white light). The fully crystallized glass is essentially opaque to light. We will take the fractional change in absorption as representing the fraction crystallized (and ignore the details of the physical theory of light scattering for the purposes of this experiment). A more detailed description of the factors affecting light absorption is given in an appendix to this manual.

*Items for the Report*

You should record all the data available to the group and any additional data that other groups make available to you (with appropriate citations). You should attempt to quantify the progress of the crystallization reaction by all the available means. The opacity is likely to be the easiest for observing the crystallization process in the form of an “S-curve” as a function of time. If possible, re-plot your data as a KJMA plot and extract the exponent ‘n’.

**Report**

1. A formal technical report will be submitted for this Experiment.
2. All text should be double-spaced with a 1 1/4” left margin for comments by the reviewer.
3. Each student is responsible for the originality of his/her technical report and the data utilized. Copying from unidentified sources such as prior reports is cheating.
4. The chief criterion of a good report is that it shall convey what the group did and learned and the conclusions the writer has individually drawn from the data in a way that is clear, concise, neat and readily interpretable by the reader. A student's report must show an understanding of the principles upon which the experiment was based. A report that is poorly organized and difficult for the instructor to follow is not likely to attract a high grade.

Your report should include an abstract, followed by sections entitled:

1. Title Page
2. Introduction,
3. Procedure
4. Results,
5. Discussion,
6. Conclusions (or Summary),
7. Acknowledgements,
8. Bibliography/References,
9. Appendices

**General Report Requirements**
(Please review before writing each report)

1. **Title Page** -- The title page, should include a title identifying the report, its author, and the names of the group members. The title itself should be concise, yet descriptive and include key words that identify the experiments and convey the message of the report. Also included on the title page is the date on which the report is actually submitted as well as the name of the instructor who supervised the experiment.

2. **Abstract** -- The abstract is simply a complete capsule report that can function independently of the body of the work. It should be 100 to 200 words in length, all in one paragraph, and should emphasize key results and conclusions, as well as interpretations and recommendations. The abstract should include a statement of the work actually done and should be written on a separate page after the rest of the report has been completed.

3. **Introduction** -- The introduction should be one or two pages in length. It should begin with a brief discussion (2 to 4 paragraphs) of the background and/or theory behind the experiment. A mere restatement of the objective found in the Handbook is not sufficient. The final paragraph in the introduction should define the scope and nature of the experiments, i.e., state very succinctly what was done.

4. **Experimental Procedure** -- The test procedure should be described concisely and should include any operational features that were discovered during the course of the experiment. For instance, time to reach steady state, length of an individual experiment and techniques used in sampling are important. The testing equipment and materials used in the project should be described in this section in sufficient detail so that they could be duplicated by the reader. Common items (balances, graduated cylinders, etc.) need not be named.

5. **Test Results** -- This is perhaps the most important part of the report, for it represents your interpretation of the results of the experiment. Even though the results may be most effectively presented in tabular or graphical form, they must be preceded by text describing them. If appropriate, an estimate of precision of the data in terms of a relative uncertainty or confidence limit should be included. References should be made in the text to figures, graphs, tables, and equations, which are inserted in the report immediately following reference to them or as the next page. An analysis of the data should be included. Sample calculations should be included and are best presented as an Appendix.

6. **Discussion** -- In this section, compare your results with theory or previous work. Discuss points of similarity or divergence and, if possible, give sources of these discrepancies. It is quite proper to include another author's curves on your plots, but not his individual data points. Evaluate trends in the results and any conclusions that can be drawn. Development of conclusions must begin in this section where they can be supported by logical argument, even though they will be dealt with exclusively in the next section. In the event of poor results, explain how the experiment should be modified to obtain satisfactory ones. This important section demonstrates your thinking and understanding of what was intended.
7A. Conclusions -- This section should be a numbered listing of the more important test results and major conclusions reached in the discussion. Conclusions are single sentences and typically 5 to 8 of them should be sufficient.

7B. Summary -- This section is a recapitulation of major points made in the Discussion in paragraph form and is intended to leave the reader with a strong impact and provide a ready reference. (Be brief but complete). You may use either a summary or conclusion section as you prefer, but not both.

8. References -- This is a list of references in alphabetical order by author.

1. Use journal abbreviations as follows (article titles need not be included):

2. References to books should include the title and pages within the book.

9. Appendices -- Detailed technical information that would slow down development of the results in the main body of the work should be included in these sections. An appendix contains information that would enable a reader to go into depth and completely check and reproduce the results. Included should be at least one complete set of sample calculations from original data to final results, copies of original data sheets, computer programs, etc. Appendices should not contain information vital to the report such as graphs or tables of data that properly belong in the Test Results section.

Report Grading
Reports will be graded on the following basis:

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Grading for reports submitted late will be reduced 20% for the first week and an additional 20% for each succeeding week.

Students are referred to the University Policy About Cheating and Plagiarism (Organization Announcement No. 297, 6116/80). It shall be the policy in this course to discourage cheating to the extent possible, rather than to try to trap and to punish. On the other hand, in fairness to all concerned, cheating and plagiarism will be treated severely.
"Cheating includes but is not necessarily limited to:
  1. Plagiarism, explained below.
  2. Submission of work that is not the student's own for reports or quizzes.
  3. Submission or use of falsified data.

Plagiarism includes (but is not limited to) failure to indicate the source with quotation marks or footnotes, where appropriate, if any of the following are reproduced in the work submitted by a student:
  1. A graph or table of data.
  2. Specific language.
  3. Exact wording taken from the work, published or unpublished, of another person."

**Technical Requirements for the Report**

Each report should include at least the following items:

1. A description of the objectives of this lab.
2. Details on the experimental procedures.
3. A record of the hardness and toughness (from crack length) measurements.
4. A record of the light transmission results.
5. A record of X-ray diffraction results, with analysis of crystalline phases and mention of the amorphous background.
6. An analysis of the results in terms of the kinetics of phase transformation up to and including KJMA analysis.
7. By combining your results with those of others, you should be able to plot the kinetics of crystallization at different temperatures.

**References:**

**Books:**

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<td>D.J. Green</td>
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<td>Mechanical Properties of</td>
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<td>Ceramics, 1998</td>
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<td>Glass Ceramic Technology</td>
<td>W. Höland and G. Beall</td>
<td>American Ceramic Society</td>
<td>1-57498-107-2</td>
<td>620.144 H72G</td>
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Appendix: Photometry of Glass Crystallization

Reference: Absorption and Scattering of Light by Small Particles
Craig F. Bohren and Donald R. Huffman, Wiley, 1983.

Transmitted Intensity

The basic equation assumes a linear relationship between the decrement in light intensity and the distance traveled by the radiation in the material:

\[ \frac{I}{I_0} = e^{-\alpha x}, \]

where \( I \) is the transmitted intensity, \( I_0 \) is the incident intensity, \( \alpha \) is the absorption coefficient (or inverse extinction length) and \( x \) is the distance traveled (thickness of the glass slab, in our case). The intensities are easily measured with a photometer by recording the readings with and without the specimen inserted in the beam. Note that our simple experiment does not distinguish between transmitted and forward scattered light. The apparatus could be improved with some lenses and a smaller pinhole at the detector.

Cross Sections for Scattering, Absorption, Extinction

The extinction of light expressed by the coefficient \( \alpha \) (which has units of m\(^{-1}\)) can be related to the number density of particles, \( N \) (units of m\(^{-3}\)), and the cross sections for scattering, \( C_{\text{scatter}} \), and absorption, \( C_{\text{abs}} \), (which have units of m\(^2\))

\[ \alpha = N(C_{\text{abs}} + C_{\text{scatter}}). \]

We will, however, ignore the distinction between scattering and absorption for the purposes of our experiment and combine the two cross sections together as an extinction cross section, \( C_{\text{ext}} = C_{\text{scatter}} + C_{\text{abs}} \). Thus we can measure extinction directly from the photometry:

\[ NC_{\text{ext}} = \ln(I_0/I)/x \]

By dividing the cross section by the particle area, one obtains an extinction efficiency, \( Q_{\text{ext}} \), which is useful under some circumstances. For spheres with radius \( r \):

\[ Q_{\text{ext}} = C_{\text{ext}} / \pi r^2 \]

We can also define a cross section per unit volume of particle, which for spheres is related to the extinction efficiency thus:

\[ C_{\text{ext}} / V = 2Q_{\text{ext}} / 4r. \]

Fraction Transformed

The challenge here is to relate the volume fraction transformed to the measured extinction. Bohren and Huffman discuss (section 11.5.4) the balance between absorption...
and scattering for small particles, as a function of wavelength. Two different limits appear to occur. For large enough particles, say greater than 10µm, the cross section per unit volume varies inversely with particle size (for all wavelengths and regardless of scattering versus absorption). We are most interested in the small particle size limit, however. For absorption, $C_{\text{ext}}/V$ is approximately constant with particle size. This leads to a particularly simple relationship to fraction transformed because it means that the particle volume, at constant number density, is proportional to $C_{\text{ext}}$. We will examine this case first and then consider scattering.

Given \( C_{\text{ext}}/V = A \), and that the volume associated with each particle, \( V_{\text{ppt}} = 1/N \), (as opposed to the volume of each particle) which defines the limit of crystallization (i.e. the particle has grown to occupy the entire volume), then we can obtain the fraction transformed, \( f \), directly.

\[
f = V/V_{\text{ppt}} = A'NC_{\text{ext}} = A'/[.]
\]

The constant \( A' = 1/A \) and has units of m (meters).

**Scattering**

If we consider the difference between scattering and absorption, then in practical terms, particles that scatter light tend to have a milky appearance whereas absorbing particles tend to be black, like ink. The glass ceramic samples become milky in appearance during crystallization which strongly suggests that they scatter light rather than absorbing it. The relationship between extinction coefficient and particle size is, in general, more complicated than for absorbing particles. In the size range that we are working in, 50-1000 nm, however, we will make the simplifying assumption that $C_{\text{ext}}/V$ is constant, which allows us to use the same analysis as above.

The next difficulty to be dealt with is that there is no limit on the extinction coefficient in the sense that the material becomes opaque. At some point in time, then, we can no longer measure any change in \( \square \) because we have reached the sensitivity limit of the photometer (i.e. there is an effective maximum in the ratio $I_0/I$). To be more specific about this limit, assume for the sake of argument that the minimum reading of the photometer is 0.1 (for a finite amount of light transmitted) and that its maximum reading is 9.99 (with no specimen interposed and a bright light source). The maximum ratio of $I_0/I = 99.9$, so $\ln(I_0/I)=4.6$. To simplify the problem, we will make a crude assumption, namely that the measurement limit (i.e. \( \ln(9.99/0.1) \) multiplied by the specimen thickness, \( x \)) is equivalent to \( f=1 \). With more powerful light sources (such that some light is still measurable at the photometer even for a completely crystallized specimen), we might hope to be able to find a plateau in the absorption coefficient which would represent a true limit in the crystallization process. In any case, our measurements are likely to be most accurate at small fractions transformed and to become less accurate as \( f \) approaches 1.

*Expected Results:*
The variation in [l] with time will be most rapid for the highest temperature and slowest for the lowest annealing temperature. The shape of the curve is expected to be “S-shaped” although non-linearities in the relationship between precipitate volume and inverse extinction length may contribute to this (as well as the practical limitations on measuring a limiting extinction length).
Appendix: text of patent citation for “S-glass”
Method of processing "BPS" glass ceramic and seals made therewith

Abstract

A glass ceramic composition, a glass ceramic-to-metal seal, and more specifically a hermetic glass ceramic-to-metal seal prepared by subjecting a glass composition comprising, by weight percent, SiO₂ (65-80%), LiO₂ (8-16%), Al₂O₃ (2-8%), K₂O (1-8%), P₂O₅ (1-5%), B₂O₃ (0.5-7%), and ZnO (0-5%) to the following processing steps: 1) heating the glass composition in a belt furnace to a temperature sufficient to melt the glass and crystallize lithium phosphate, 2) holding at a temperature and for a time sufficient to create cristobalite nuclei, 3) cooling at a controlled rate and to a temperature to cause crystallization of lithium silicates and growth of cristobalite, and 4) still further cooling in stages to ambient temperature. This process produces a glass ceramic whose high coefficient of thermal expansion (up to 200.times.10⁻⁷ in/in./°C.) permits the fabrication of glass ceramic-to-metal seals, and particularly hermetic glass ceramic seals to nickel-based and stainless steel alloys and copper.

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References Cited [Referenced By]

U.S. Patent Documents

2392314
Jan., 1946
Dalton 106/54.

3220815
Nov., 1965
McMillan et al. 65/32.

3564587
Feb., 1971
Ellis 161/93.

4414282
Nov., 1983
McCollister et al. 428/433.

4536203
Aug., 1985
Kramer 65/29.

4921738
May., 1990
Cassidy 428/34.
What is claimed is:

1. A method for making a bubble-free glass composition comprising: mixing, by weight, ingredients comprising about 63.0% SiO$_2$, about 22.3% Li$_2$CO$_3$, about 4.4% Li$_3$PO$_4$, about 3.2% Al$_2$O$_3$, about 3.7% K$_2$CO$_3$, about 1.8% H$_3$BO$_3$, and about 1.6% ZnO; melting the mixed ingredients while stirring at elevated temperature in air, of less than 25% relative humidity, for a time sufficient to form a homogeneous glass melt; allowing the glass melt to flow whereby bubbles in the melt rise to the surface and burst; and allowing the glass melt to solidify to a bubble-free glass composition comprised of, by weight %, 74.4% SiO$_2$, 3.8% Al$_2$O$_3$, 1.2% B$_2$O$_3$, 3.15% P$_2$O$_5$, 2.95% K$_2$O, 12.65% Li$_2$O, and 1.85% ZnO.

2. A product made by the method of claim 1.

3. A product made by the method of claim 1 prepared from phosphates, carbonates, or borates which are functionally equivalent to the phosphates, carbonates, and borates of claim 1.

4. A method for making bubble-free preforms from the bubble-free molten glass of claim 1 comprising: pouring the molten glass into the center cavity of a preheated mold; squeezing the molten glass into runners in the mold with a plunger; allowing the molten glass to solidify; removing the solidified glass from the mold and annealing it at about 460 degree C. for about one hour; and cutting the solid glass to desired preform lengths.

5. A product made by the method of claim 4.

6. A method for making bubble-free billets from the bubble-free molten glass of claim 1 comprising: pouring the molten glass into a billet mold; allowing the molten glass to solidify and further cool until the center of the billet is almost free of red color; removing the solidified glass from the mold and stabilizing the temperature throughout the billet in an oven; and cooling the billet slowly to room temperature to reduce stress in the billet.


8. A method for making bubble-free glass cullet from the bubble-free molten glass of claim 1 comprising pouring the molten glass between water-cooled stainless steel rollers, pouring the molten glass in thin sheets onto a cold metal plate or into water thereby solidifying the glass and causing it to break under thermal stress into small pieces or cullet.

9. A method for making pressed-powder preforms from the glass cullet of claim 8 comprising: grinding the cullet into powder; sieving the powder to obtain a uniform particle size; mixing the powder with a binder; compacting the powder/binder mixture to the desired shape and dimensions of the preform; and sintering the compact to burn away the binder and melt the glass particles such that the density of the preform is about 90% to about 95% that of the solid glass.
10. A product made by the method of claim 9.

11. A method of making a glass ceramic from a solid glass composition consisting of, by weight %, 73.5-74.9% SiO$_2$, 3.3-4.2% Al$_2$O$_3$, 1.0-2.5% B$_2$O$_3$, 2.45-3.35% P$_2$O$_5$, 2.7-3.6% K$_2$O, 12.3-13.9% Li$_2$O, and 0-2.2% ZnO comprising: melting the glass composition by heating it to about 950\degree C.-1050\degree C. C. causing crystallization of Li$_3$PO$_4$ necessary for the nucleation of cristobalite from the glass composition, thereby forming first-precursor glass ceramic; holding the first-precursor glass ceramic at a temperature of between 950\degree C.-1050\degree C. C. for sufficient time to create cristobalite nuclei, thereby forming second-precursor glass ceramic; cooling the second-precursor glass ceramic to a temperature of between 750\degree C.-775\degree C. C. at a controlled rate of about 5\degree C.-25\degree C. C./min to cause crystallization of lithium silicates and growth of cristobalite, thereby forming the final glass ceramic product; further cooling the final glass ceramic product to about 580\degree C. C. at a cooling rate of about 25\degree C./min; and still further cooling the final glass ceramic product at a controlled rate to ambient temperature producing a glass ceramic with a the coefficient of thermal expansion of from about 120.x10$^{-7}$ in/in/\degree C. to about 200.x10$^{-7}$ in/in/\degree C.

12. A product made by the method of claim 11.

13. The method of claim 11 wherein the first-precursor glass ceramic is held at about 1000\degree C. C. for about 15 min.

14. The method of claim 11 wherein the second-precursor glass ceramic is cooled to about 750\degree C. C. at a rate of about 10\degree C./min.

15. A product made by the method of claim 11 wherein the coefficient of thermal expansion is about 145.x10$^{-7}$ in/in/\degree C.

16. The method of claim 11 wherein the solid glass composition is in the form of a pressed-powder glass preform.

17. The method of claim 11 wherein the solid glass composition is in the form of a solid glass billet.

18. The method of claim 11 wherein the solid glass composition is in the form of a solid glass preform.

19. A method for making a hermetic seal, in a traveling belt furnace, between a glass ceramic of claim 11 and a metal or a metal alloy, both having substantially the same coefficient of thermal expansion, comprising: melting a glass composition of claim 11 by heating the glass composition and metal or metal alloy, in mutual contact, to about 950\degree C.-1050\degree C. C. while they pass through the furnace temperature-sealing zone, causing crystallization of Li$_3$PO$_4$ necessary for the nucleation of cristobalite from the glass composition, thereby forming first-precursor glass ceramic; holding the first-precursor glass ceramic and a metal or metal alloy at a temperature of between 950\degree C.-1050\degree C. C. for sufficient time to create cristobalite nuclei in the first-precursor glass ceramic, thereby forming second-precursor glass ceramic; cooling the second-precursor glass ceramic and a metal or metal alloy to a temperature of between 750\degree C.-775\degree C. C. at a controlled rate of about 5\degree C.-25\degree C. C./min to cause crystallization of lithium silicates and growth of cristobalite in the second-precursor glass ceramic, thereby forming the final glass ceramic product; further cooling the final glass ceramic product and a metal or metal alloy to about 580\degree C. C. at a cooling rate of about 25\degree C./min; and still further cooling the final glass ceramic product and a metal or metal alloy at a controlled rate to ambient temperature.

20. A product made by the method of claim 19.

21. The method of claim 19 wherein the metal alloy is Inconel 718.

22. The method of claim 19 wherein the metal alloy is Inconel 625.
23. The method of claim 19 wherein the metal alloy is Hastelloy.

24. The method of claim 19 wherein the metal alloy is Haynes Alloy 242.

25. The method of claim 19 wherein the metal alloy is stainless steel.

26. The method of claim 19 wherein the metal alloy is nitronic steel.

27. The method of claim 19 wherein the metal is copper.

28. A glass ceramic-to-metal alloy hermetic seal product made by the method of claim 19 wherein the metal alloy is Inconel 718.

29. A glass ceramic-to-metal alloy hermetic seal product made by the method of claim 19 wherein the metal alloy is Inconel 625.

30. A glass ceramic-to-metal alloy hermetic seal product made by the method of claim 19 wherein the metal alloy is Hastelloy.

31. A glass ceramic-to-metal alloy hermetic seal product made by the method of claim 19 wherein the metal alloy is Haynes Alloy 242.

32. A glass ceramic-to-metal alloy hermetic seal product made by the method of claim 19 wherein the metal alloy is stainless steel.

33. A glass ceramic-to-metal alloy hermetic seal product made by the method of claim 19 wherein the metal alloy is nitronic steel.

34. A glass ceramic-to-metal hermetic seal product made by the method of claim 19 wherein the metal is copper.

35. A method of precipitation-hardening the Inconel 718 of the glass ceramic-to-Inconel 718 hermetic seal product of claim 28 to strengthen the Inconel 718 without compromising the seal, comprising: a. heating the seal in a batch furnace at from about 700 degree C to about 750 degree C for about one to about 8 hours; b. lowering and maintaining the temperature of the seal at from about 595 degree C to about 645 degree C for about one to about 8 hours; and c. cooling the seal to ambient temperature.

36. The method of claim 19 wherein the glass composition is in the form of a solid glass preform.

37. The method of claim 19 wherein the glass composition is in the form of a pressed powder preform.

38. An electrical header product made by the method of claim 19 wherein the glass composition is in the form of a solid glass preform.

39. An electrical header product made by the method of claim 19 wherein the glass composition is in the form of a pressed powder preform.

Description

BACKGROUND OF THE INVENTION

This invention relates to an improved method for glass ceramic-to-metal seals and particularly hermetic glass ceramic seals to nickel based and stainless steels alloys using a "traveling, continuous belt" (hereinafter referred to as "belt") furnace for processing U.S. Pat. No. 2,392,314 to Dalton discloses glass
material for matched thermal expansion sealing to molybdenum and alloys of iron, nickel, and cobalt metal
wherein the amount of Li$_2$O in the glass composition is only 0.8%.

U.S. Pat. No. 3,220,815 to McMillan et al. discloses a devitrified glass (glass ceramic) having an
coefficient of thermal expansion (CTE) of 142 times 10$^{-7}$ in/in/°C. This can be used for sealing
to Mesmeric steel having a CTE of 140 times 10$^{-7}$ in/in/°C. The glass contains 10-59% ZnO in
addition to Li$_2$O and SiO$_2$.

U.S. Pat. No. 3,564,587 to Ellis discloses a complex glass composition suitable for sealing to low CTE
glasses and metals.

U.S. Pat. No. 4,414,282 to McCollister et al. discloses a high CTE glass ceramic (S glass ceramic) similar
to, but not the same as, that of the present invention. McCollister uses either a four-step or six-step batch-
process heat treatment (meaning the parts remain stationary in the furnace as distinct from moving through
the furnace with defined temperature zones on a traveling belt) of the glass compositions rather than the
belt processing taught in the present invention. The CTE of McCollister's glass ceramic is 120 to
160 times 10$^{-7}$ in/in/°C. with a preferred CTE of 145 times 10$^{-7}$ in/in/°C., whereas
the CTE of the BPS glass ceramic of the present invention is 120 to 200 times 10$^{-7}$ in/in/°C.
with, for example, a preferred CTE of 145 times 10$^{-7}$ in/in/°C. for seals to Inconel and a CTE
of 165 times 10$^{-7}$ in/in/°C. for seals to stainless steels. McCollister's glass ceramic composition,
when processed according to the present invention, will not have the desired high CTE or the crystalline
structure which contains cristobalite. The crystalline microstructure of the glass ceramic composition of the
present invention is the same as that taught by McCollister.

US Pat. No. 4,536,203 to Kramer discloses control of the CTE in hermetic glass ceramic-to-metal seals not
only by batch heat treatment but also heat treating using pressures up
to 22,000 psi.

US. Pat. No. 4,921,738 to Cassidy discloses an improved high CTE glass ceramic interface for sealing to
metals. Cassidy uses a glass ceramic composition within McCollister's preferred compositional range, and
McCollister's batch four step heat treatment. However Cassidy uses metals other than Inconel 718 or
Inconel 625.

Borom et al. in the Journal of the American Ceramic Society 58, 385-391 (Sept.-Oct., 1975) discloses a
glass composition, the ingredients of which are similar to those of the present invention, but which are not
useful as sealants to metals of the present invention.

effect on chemical stability of alumina and zinc oxide on the silica-rich phase of glass ceramics.

SUMMARY OF THE INVENTION

Nickel base alloys such as Inconel 718, Inconel 625, and Hastelloy C are particularly suitable for sealing
with certain known hard borosilicate glasses because, with respect to their expansion characteristics, these
alloys more nearly resemble the glasses than other previously employed sealing materials.

In making a strong chemical bond between a metal and a glass or glass ceramic, it is not only essential that
the expansion characteristics of the alloy and the glass be sufficiently well matched to reduce residual stress
in the seal, but it is equally desirable that the glass have the highest possible corrosion resistance. It is also
important that the melting temperature of the glass be sufficiently low to permit production of the glass or
glass ceramic in conventional furnaces. It is also desirable that the expansion and viscosity be such that the
glass is capable of sealing to nickel-base alloys and stainless steels. It is further desirable that the glass have
a high mechanical strength so that the hermetic seal can withstand high external stresses.

The prior-art glasses used for sealing with nickel based alloys have not been satisfactory in all respects and,
although certain desirable properties may be obtained at the sacrifice of others, no single glass possesses all
of the above-mentioned desirable properties except that described by McCollister. No prior glass or glass
ceramic has been entirely satisfactory for sealing to stainless steels.

Today most hermetic glass-to-metal seals are manufactured in belt furnaces. These hermetic devices cannot
withstand high temperatures or high stresses. High CTE glass ceramics sealed to Inconels and Hastelloys
can withstand high temperatures and high stresses, but these seals must be manufactured in batch furnaces.
in order to closely follow the prescribed thermal treatment necessary to nucleate and grow the desired crystal phases. These batch furnaces are not usually used by glass-to-metal seal manufacturers.

Belt-processable S (BPS) glass ceramic (as distinguished from S glass ceramic made in a batch furnace), through the process disclosed in the present invention, forms hermetic high-strength seals to Inconel, Hastelloy, Haynes alloys, and copper. High-strength seals can also be made using 304 stainless steel as well as nitronic steel bodies, and 303 or 333 stainless steel pins with the disclosed glass ceramic of the present invention by belt processing. Hermetic seals should also be possible using BPS glass ceramic and the metal alloys disclosed by Cassidy. The thermal treatment of the glass ceramic of this invention is critical to the formation of the necessary crystal phases, especially the time and temperature in the melt zone of the belt furnace and the cooling rate to 700. to 750.degrees C.

An object of the present invention is to make high-performance glass ceramic hermetic seals to high-CTE metals.

A further object of the present invention is to preferably make these seals in a belt furnace but in a batch furnace as well.

A still further object of the present invention is to use pressed powder preforms as the source of the glass ceramic rather than solid glass preforms.

A still further object of the present invention is to provide drop-in glass ceramic replacements for conventional glass preforms.

A still further object of the present invention is to improve the reliability, strengths and performance of hermetically sealed devices with improved corrosion resistance and thermal shock resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and form part of the specification, illustrate embodiments of the present invention and, together with the description, serve to explain the principles of the invention.

FIG. 1 is a graph representing the crystallizing temperature profile which is typically employed in a belt furnace used in the preparation of the device of FIG. 4B.

FIG. 2 is a section view of a cast iron mold used to prepare solid glass preforms from molten glass.

FIG. 3 is a partially broken away perspective view of a hermetic electrical header incorporating a glass ceramic seal with a body of a metal shell wherein said seal is obtained by the use of solid glass preforms.

FIG. 4 is a section view of an electrical header prior to sealing with a glass ceramic pressed powder preform.

FIG. 5 is a section view of an electrical header which has been sealed with a glass ceramic.

DETAILED DESCRIPTION OF THE INVENTION

Glass ceramic compositions containing, by weight, SiO.sub.2 (65-80%), Al.sub.2 O.sub.3 (2-8%), B.sub.2 O.sub.3 (0.5-7%), P.sub.2 O.sub.5 (1-5%), K.sub.2 O (1-8%), Li.sub.2 O (8-16%), and ZnO (0-5%) are particularly suitable for sealing with the nickel-base alloys, stainless steels, and copper, have a better chemical durability and mechanical strength than prior glasses and glass ceramics used for this purpose, and are easier to manufacture than prior glass ceramics.
In Table I preferred examples of the BPS-glass ceramic compositions falling within the scope of the present invention are given in weight percent as calculated from their respective batches, as well as prior S-glass ceramics used by McCollister for sealing nickel-base alloys.

The compositions in Table 1, being calculated from their respective batches, are not exactly the compositions of the final glass ceramics because there are small indeterminate losses during the glass melting.

**TABLE I**

<table>
<thead>
<tr>
<th>Glass Ceramic</th>
<th>S</th>
<th>BPS</th>
<th>Wt % Range</th>
<th>Preferred Wt % Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>71.7</td>
<td>74.4</td>
<td>65-80</td>
<td>70-80</td>
</tr>
<tr>
<td>Li(_2)O</td>
<td>12.6</td>
<td>12.65</td>
<td>8-16</td>
<td>12-14</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>5.1</td>
<td>3.8</td>
<td>2-8</td>
<td>3.3-4.2</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>4.9</td>
<td>2.95</td>
<td>1-8</td>
<td>1.6-3.6</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>2.5</td>
<td>3.15</td>
<td>1-5</td>
<td>2.5-3.5</td>
</tr>
<tr>
<td>B(_2)O(_3)</td>
<td>3.2</td>
<td>1.2</td>
<td>0.5-7</td>
<td>0.75-2.5</td>
</tr>
<tr>
<td>ZnO</td>
<td>0</td>
<td>1.85</td>
<td>0-5</td>
<td>0-3.0</td>
</tr>
</tbody>
</table>

In preparing the sealing glasses of the disclosed compositional range, the batch ingredient powder raw materials are intimately mixed by hand or in a commercially available blender, and heated to such temperatures while stirring that all of the raw materials are converted to either glass-forming or glass-modifying oxides, thereby enabling the formation of a glass from a homogeneous melt.

Generally, the batch ingredients are mixed well in a blender, and melting is done in a 100% platinum crucible or a 90% platinum--10% rhodium crucible in an electric furnace at a temperature of about 1550 degree C. in air of less than 25% relative humidity (the lower the better) with continuous stirring. After stirring for about 15 hr the glass is fined, i.e., trapped bubbles are allowed to float to the top of the molten glass where they burst.

The batch materials employed for preparing the glasses of the present invention are of a high purity and selected from commercially available materials. The components of the batch may be in the form of functionally equivalent phosphates, carbonates, borates or any other form which does not adversely affect the subject glass composition.

Glass having a composition as described above, prepared by the melting together of the components of a batch will not, by simple cooling to solidification, possess the necessary CTE which will match that of the nickel base, stainless steel alloys, or copper to which it is intended to be sealed. In order to obtain the desired CTE in the final glass ceramic seal, it is necessary to subject the glass to the following heat treatment in either a belt furnace or a batch process:

a. melting the glass, allowing it to flow and come into contact with the metal components, and crystallizing Li\(_{\text{sub.3}}\) PO\(_{\text{sub.4}}\) from the fluid above 950 degree C which is accomplished while the glass travels through the furnace sealing zone;
b. holding the crystalline glass ceramic at 950.\degree.-1050.\degree. C., preferably 975.\degree.-1025.\degree. C. and most preferably 1000.\degree. C. for 5-60 min, preferably 10-30 min, and most preferably 15 min, thereby creating Li.sub.3 PO.sub.4 which nucleates cristobalite, and forming a bond between the glass ceramic and metal components while the glass, metal components, and/or mold travel through the hot zone of the furnace;

c. cooling to about 750.\degree.-775.\degree. C. at a controlled rate of about 5.\degree.-25.\degree. C./min, causing crystallization of lithium silicates and growth of cristobalite;

d. cooling to about 580.\degree. C. at a rate of about 25.\degree. C./min producing glass ceramic material of the desired CTE; and

e. cooling further to room temperature at about 5.\degree.-25.\degree. C./min.

When Inconel 718.TM. (a nickel-chromium-iron alloy sold by Huntington Alloys) is used as a metal to which the glass ceramic material is bonded, the Inconel 718 may be subjected to an additional precipitation hardening treatment to form an exceptionally high-strength product. The precipitation hardening treatment is preferably a two-step treatment performed in a batch furnace including the steps of maintaining the temperature of the product at 700.\degree.-750.\degree. C., preferably 725.\degree. C. for 1-8 hr, preferably 2 hr, and thereafter lowering and maintaining the temperature of the product at 595.\degree.-645.\degree. C., preferably 620.\degree. C., for 1-8 hr, preferably 2 hr. This precipitation-hardening treatment is not detrimental to the properties of the glass ceramic and can be performed after sealing and cooling in the belt furnace.

Careful control of the heat-treatment process, especially the cooling rate of the glass after sealing of the BPS glass ceramic at 1000.\degree. C. (FIG. 1), is required to obtain the desired phase assemblage and CTE of 120 to 200. times. 10.sup.-7 in/in/.degree.C. or 165. times. 10.sup.-7 in/in/.degree.C. The glass ceramic contains crystalline phases of lithium metasilicate (Li.sub.2 O.SiO.sub.2), nucleant Li.sub.3 PO.sub.4, cristobalite solid solution (SiO.sub.2 SS), and minor amounts of lithium disilicate (LiO.sub.2.2SiO.sub.2). It also contains a residual glass phase, rich in oxides of potassium, aluminum, zinc, and silicon. The presence of cristobalite in the phase assemblage is essential in obtaining a high CTE for the BPS glass ceramic. The presence of zinc oxide aids the corrosion resistance of the glass ceramic and the glass-to-metal bond strength. Thermal treatment of the glass at temperatures outside the range of 950.\degree.-1050.\degree. C., where Li.sub.3 PO.sub.4 doesn't form, as compared with 1000.\degree. C., does not provide adequate quantities of cristobalite to produce the necessary high CTE.

The following examples are representative embodiments and uses of a glass composition of the present invention.

EXAMPLE 1

The constituent raw materials (approx. 1200 g) of Table 2 are introduced into a twin-cone blender and mixed for about 60.+-.10 min.

<p>| TABLE 2 |
|-----------------|-----------------|
| Finished Raw Material | Weight (g) Product Composition (wt %) |
| SiO.sub.2 | 744.00 | SiO.sub.2 | 74.40 |
| Li.sub.2 CO.sub.3 | 263.62 | Li.sub.2 O | 12.65 |</p>
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>Mass (%)</th>
<th>Chemical</th>
<th>Formula</th>
<th>Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li&lt;sub&gt;3&lt;/sub&gt;PO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>52.01</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>38.00</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>3.15</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.80</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>44.00</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.95</td>
</tr>
<tr>
<td>H&lt;sub&gt;3&lt;/sub&gt;BO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>K&lt;sub&gt;2&lt;/sub&gt;CO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>21.32</td>
<td>ZnO</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.20</td>
</tr>
<tr>
<td>ZnO</td>
<td>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>18.50</td>
<td></td>
<td>ZnO</td>
<td>1.85</td>
</tr>
</tbody>
</table>

The resultant mixture may be stored in a covered beaker in a desiccator, or in a drying oven maintained at 125±10°C for a maximum of about seven days prior to use. The glass powder is then melted according to the following procedure:

a) the glass powder is added batchwise to a crucible in a furnace at about 1550°C, in dry air, and the temperature is allowed to stabilize at about 1550°C after each addition of powder until all the powder has been added and melted;
b) the glass melt is stirred with a platinum stirrer continuously at about 125 rpm for about 15 hr at 1550±10°C;
c) the stirrer is removed and the glass is fined for about 15 min;
d) if bubbles appear in the melt, the glass is allowed to fine further until all the bubbles have disappeared; and
e) the glass is processed according to Example 2 or Example 3, below.

**EXAMPLE 2**

Example 2 is representative of the preparation of solid glass preforms, solid glass billets, or glass cullet using the glass composition of the present invention.

Solid glass preforms are prepared using the molten glass from Example 1 and the mold from FIG. 2. The bubble-free molten glass is poured into the center cavity 20 of a preheated mold 21, preferable cast iron, and then squeezed into runners 22 in the mold 21 with a plunger 23, preferably cast iron. The glass assumes the shape of the runner cavity 22. This shape can be a cylinder, half cylinder, or more usually, a half cylinder with a depression on the flat side of the cylinder to allow for pin clearance when two of these preforms are mated together. These glass shapes are removed from the mold and placed in an annealing oven at 460°C for typically one hour. These glass pieces are then cut to desired length yielding solid glass preforms.

Solid glass billets are prepared using the molten glass from Example 1. The bubble-free molten glass is poured into the billet mold and allowed to cool until the red color is almost gone from the center of the billet. The glass is removed from the mold and placed in an oven to first stabilize its temperature, and then slowly cooled to room temperature to reduce stress in the billet.

Glass cullet is prepared using the molten glass from Example 1. The bubble-free molten glass is poured between water-cooled stainless steel rollers, poured in thin sheets onto a cold metal plate which can be copper or cast iron, or it is poured into water. In any case the glass cools quickly, breaking into small pieces known as cullet; the cullet is not annealed.
EXAMPLE 3

Example 3 demonstrates the preparation of a pressed powder preform useful in many sealing applications. The BPS glass ceramic cullet from Example 2 is ground into a powder and sieved to obtain a uniform particle size. The glass powder is then mixed with any number of binders. It is compacted with a hydraulic press in a die to form the desired shape and dimensions of the pressed powder preform. The pressed powder preform with binder is sintered in a furnace to first burn out the binder, and then to melt the glass particles such that the density of the preform is approximately 90-95% that of a solid glass.

EXAMPLE 4

Example 4 is directed to the preparation of a header, as shown in FIG. 3, which contains a glass ceramic seal between a Hastelloy.TM. "hairpin" 30 and the Inconel 625.TM. body 31 of a header. The bottom fixture 32 contains a pair of longitudinal recesses. A tubular carbon insert 33 is pressed into each recess, leaving a small boss of carbon exposed above the fixture. The unit of FIG. 3 is assembled by placing a metal header body 31 on the bottom metal fixture 32, insuring that the two carbon bosses are engaged in the through holes in the header body 31. The lower ends of the hairpin 30 are then inserted into each of carbon inserts 33. The hairpin 30 contains a bent portion 34 in each leg. The solid glass preforms 35 from Example 2 are then placed on either side of hairpin 30. The header assembly of FIG. 3 is then subjected to heat treatment in a belt furnace capable of providing the thermal profile in FIG. 1.

The heat-treated, crystallized units are then removed from the furnace for disassembly and the header body is removed from the bottom fixture 32. Prior to electropolishing and grinding, the headers are inspected and tested. The glass ceramic in the connector end of the header is inspected under 10-20.times. magnification. Evidence of cracks in the glass ceramic is cause for rejection. The header is tested with a helium leak detector and any detectable leak is cause for rejection.

The metal parts are electropolished using a variable DC power supply with a stainless steel beaker as the anode and the metal part the cathode. The electropolishing solution is prepared by adding one part of concentrate (Electro-Glo 300.TM.) to three parts by volume phosphoric acid (85% grade). The electropolishing operating voltage is 5-9 volts and the temperature of the solution is maintained at approximately 49.degree.-54.degree. C. The solution should not be overheated as etching of the metal occurs at approximately 66.degree. C. Electropolishing is conducted for a total of 3 min, and the part is rinsed with tap water.

A cavity in the top of the header is ground out with a diamond burr, removing the 180.degree. bend in the hairpin 30, to form two individual pins which are properly spaced and sealed within the header. The bent portions of the hairpin together with the glass ceramic seal allow the space between the ground-off ends of the hairpin to be precisely fixed.

EXAMPLE 5

Example 5 is directed to the preparation of a header, as shown in FIG. 4, which contains a glass ceramic seal between a 330 stainless steel pin 40 and a 304 stainless steel body 41. The body 41 and pins 40 are cleaned ultrasonically in a 10-vol% solution of Oakite NST.TM. and water for about 10 min, and then rinsed in flowing deionized water for about 1 min followed by ultrasonic cleaning in deionized water for about 2 min. The deionized water is replaced with reagent grade 1-propanol, followed by ultrasonic agitation for an additional 1 min. The body 41 and pins 40 are then dried under an infrared heat lamp.

The bottom cylindrical carbon inserts 42 are placed in the base fixture 43 to insure that the step side 44 of the carbon 42 insert is facing up. The header body 41 is lowered on the base fixture 43 so that the through holes 45 in the body 41 capture the carbon inserts 42. One pin 40 is placed into each carbon insert 42 with the large flat in the pin 46 up. Two half-cylinder BPS pressed powder preforms 47 are placed in the through hole 45 in the body 41 and around the pin 40. This is repeated for the other three body holes 45 and pins 40. Each cylindrical top carbon insert 48 is placed over the large flat end 46 of the pins 40. Once the flats 46 on the pins 40 are rotated to the desired alignment, the top fixture 49 is lowered over the pin flats 46.
The header assembly is placed on a quartz plate, covered by an inverted quartz sealing boat, and placed on the belt at the entrance to the furnace. The belt furnace is a Transheat Model TCA64-10-90N72.TM. manufactured by BTU Engineering Corp. The furnace sealing parameters are as follows:

- a) the first 5 zones are set at 1020 degree C;
- b) the next 5 zones are set at 780 degree C;
- c) the belt speed is 2 in/min; and
- d) the three nitrogen cover gas Transheat.TM. flowmeter settings are each set at 50.

Upon exit from the furnace, the mold assembly is disassembled and the sealed header (FIG. 5) is inspected under 10-70 times magnification for defects such as non-wetting on cracks in the glass ceramic 51, or pieces of carbon mold broken off between the header body 41 and pin 40. The sealed header in FIG. 5 is then tested for hermeticity with a helium leak detector.

The oxide on the metal parts is chemically removed by soaking for about 10 min in an approximately 96 degree C-99 degree C. solution containing 20 g potassium permanganate, 200 g sodium hydroxide, and 400 ml deionized water. The sealed headers are then rinsed in deionized water and dried.

EXAMPLE 6

Example 6 teaches the control of thermal expansion of the BPS glass ceramic by varying the belt furnace processing conditions. The glass ceramic composition is from within the preferred range (Table I).

Pieces of solid glass about 1.5 in long are placed in a carbon mold used to make samples for thermal expansion measurements. The mold and glass are placed on a quartz plate, covered by an inverted quartz sealing boat and placed on the belt as in Example 5. The furnace-sealing parameters are as follows:

- a) the first 4 zones are set at 1020 degree C.; and
- b) the next 6 zones are set at 780 degree C.

Three separate runs are made with belt speeds of 3, 4, and 4.5 in/min.

Each sample of the resulting BPS glass ceramic is cut to a 1-inch length with the ends parallel using a modified Buehler Isomet.TM. saw fitted with two diamond impregnated blades spaced 1 inch apart. Each 1-inch long glass ceramic sample in turn is cleaned and placed on the sample side of a Theta Dual-Push Rod Dialatometera.TM. fitted with a 0.5%-accuracy measuring head. The Theta furnace is rolled over the quartz sample assembly and the BPS glass ceramic is heated at a rate of 2.5 degree C/min to 600 degree C. The CTE is calculated from room temperature to 250 degree C., 460 degree C., and 580 degree C, and is shown in Table 3.

<table>
<thead>
<tr>
<th>Belt speed (in/min)</th>
<th>250 degree C.</th>
<th>460 degree C.</th>
<th>580 degree C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>202</td>
<td>165</td>
<td>163</td>
</tr>
<tr>
<td>4</td>
<td>184</td>
<td>153</td>
<td>152</td>
</tr>
<tr>
<td>4.5</td>
<td>168</td>
<td>143</td>
<td>144</td>
</tr>
</tbody>
</table>

TABLE 3

CTE (10.sup.-7 in/in/.degree.C.) based on belt speeds at sealing temperatures
The compositions and methods discussed above may be utilized to bond a variety of products. The compositions and methods of the present invention are particularly useful for preparing products which are subjected to high temperatures and/or high pressures, or require inexpensive, easily machined stainless steels for volume production of electronic components via belt furnace processing. Furthermore, if Inconel 718 precipitation-hardened headers are desired for component strength, the Inconel may be precipitation hardened in a batch furnace prior to the sealing process.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of this invention.