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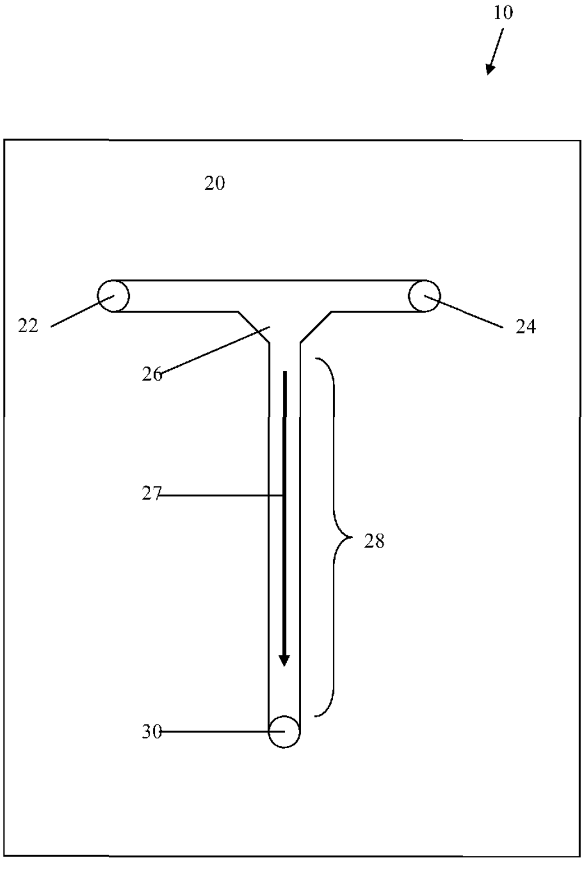
(54) Title: CRYSTALLIZATION-RESISTANT GLASS COMPOSITIONS SUITABLE FOR MANUFACTURING GLASS FRITS FOR MICROREACTORS



(57) Abstract: The invention is directed to a glass composition that can be used to make glass frits suitable for use in the manufacturing of microreactors. The glass compositions, after final sintering to produce a finished microreactor, have a surface crystalline layer of 30 µm or less, or are completely amorphous throughout. Generally, the borosilicate glasses of the invention have a composition Of B_2O_3 = 12-22 mol %; SiO_2 = 68-80 mol % and additional components selected from the group consisting of either (a) Al_2O_3 = 3-8 mol % and Li_2O = 1-8 mol %, or (b) K_2O = 0-2 mol % and Na_2O = 0- 2-ol %, except that both K_2O and Na_2O cannot both equal zero at the same time. One borosilicate glass has a composition, in mole percent (mol%) of B_2O_3 = 18-22 mol %, SiO_2 = 75-80 mol %, K_2O = 0-2 mol %, and Na_2O = 0-2 mol %, except that both K_2O and Na_2O cannot both equal zero at the same time.

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CRYSTALLIZATION-RESISTANT GLASS COMPOSITIONS SUITABLE FOR MANUFACTURING GLASS FRITS FOR MICROREACTORS

Field of the Invention

[0002] The invention is directed to crystallization-free glass frits that are suitable for the manufacturing of glass microreactor using micro-molding technology and to the glass compositions used to make such frits; and in particular to glass frits that exhibit resistance to thermal shock and have excellent chemical durability.

Background of the Invention

[0003] As a result of economic forces, environmental considerations, waste disposal regulations and other factors, activities in the fields of thermal and chemical process engineering have gravitated toward the use of microreactors for research and development, including modeling studies and chemical reactions. In addition, microreactors are finding application in pharmaceutical and biological research, development and analysis. A microreactor is a device that enables chemical reactions, either gaseous or liquid, to be done on the low milliliter scale (5-10 ml) as opposed to earlier laboratory "bench top" or pilot plant scales that varied in size from many tens of milliliters to liters in the former and up to a hundred liters, or more, in the latter. The microreactor is generally a continuous flow reactor that brings the reaction components together in a small reactor channel. Figure 1 is a top view illustrating one of the simplest designs, a "T-shaped" microreactor 10. In a typical reactor of this design a T-shape is etched into a plate 20 to a selected depth (for example, 50 μm deep by 100 μm wide) and the etched plate is then covered with another plate (14 in Figure 2) so that the etched portion form an enclosed channel. The cover plate has openings (three illustrated in Figure 1) so that fluids (gaseous or liquid) can be added and removed from the reactor. A reaction is carried out by pumping a first fluid containing a first reactant through opening 22 and a second fluid containing a second reactant through opening 24. The fluids are pumped at the same rate so that they meet at the position 26, the top of the vertical part 28 of the T where they begin to mix and react as they proceed (illustrated by the broad arrow) down the vertical part 28 of the T. The reaction product is removed at the opening 30. Figure 2 is a side view illustrating etched plate 20, top plate 14, openings 22, 24 and 30, and fluid illustrated as light grey in the reactor. The dashed line 16 illustrates the junction of plates 14 and 20.

[0004] While the simple design illustrated in Figure 1 is satisfactory for some reactions, for others a more complex design is required. For example, it may be desirous to add mixing baffles; openings for the further addition of reactants as the fluids travel from the beginning to the end of the reactor; space for heating and/or cooling elements with their associated connections; thermocouples and their connections; and other elements as may be need to carry out, control or monitor the reactions that occur within the microreactor. As a result the design of the reactor can become quite complicated; which in turn means that the construction of the reactor itself becomes complicated and expensive if etching techniques are used to construct parts of the microreactor. In addition, while materials such as metals, silicon and certain polymers can be used to fabricate microreactors, these materials are not well suited for chemical reactions at high temperature and/or that use corrosive reactants. As a result of the foregoing problems, a simplified method for making microreactors is desirous; and it is further desired that such reactors be made of glass or ceramic materials due to their high thermal stability and their chemical durability and/or inertness to the vast majority of chemicals and solvents.

[0005] As a result of the foregoing problems, methods of making microreactors using “frits”, particularly glass frits, have been developed. A frit is a powdered glass that sinters to form a structure that incorporates, for example, microreactor features and/or elements. To make the microreactor the frit is typically sandwiched between two substrate layers that may themselves incorporate some microreactor elements such as the openings for reactant(s) entry and exit, control leads for heaters and other elements, some of which have been described above. The resulting “sandwiched” microreactor must be “fluid tight” so that reactants and/or solvents do not escape. Commonly owned U.S. Patent Application Publication No. 2004/0152580 A1 (assigned to Corning Incorporated) describes borosilicate glass compositions and their use to make microfluidic devices such as the microreactors described above. As mentioned in U.S. 2004/0152580 A1, the problem with PYREX® glass frits is that they undergo devitrification (that is, crystals of different materials are formed) during sintering at temperatures in the range of 700-800 °C. However, there is a lowering of mechanical strength due to both the formation of crystals with a high coefficient of thermal expansion and the volume change that is associated with the phase transformation of cristobalite crystals at approximately 200 °C. This can lead to frit cracking on cooling after sintering. As a result, the inventors in

U.S. 2004/0152580 A1 proposed that alumina be added to the borosilicate glass composition. The addition of alumina causes the sintering ability of the frit to decrease and reduces the fluidity of the frit. While the materials describes in U.S. 2004/0152580 A1 resulted in an improved frit material, further improvements are needed to both frit compositions and to the method of making frits that can be used in microreactors. The present invention is directed to improved compositions that can be used to make glass frits that can be used in microreactor and the methods of making such frits.

Summary of the Invention

[0006] The invention is directed to glass compositions having a low softening, point low CTE, high acid and alkali chemical resistance, and high crystallization resistance that are suitable for manufacturing glass frits for microreactors. The glasses of the invention are borosilicate glasses containing either (a) lithium oxide plus aluminum oxide or (b) sodium oxide or potassium oxide. The glasses of the invention have a crystallized depth layer, as measured by the HTS method described herein using bulk glass, of less than 30 μm, preferably less than 20 μm, and most preferable 10 μm or less. The substrates used in practicing the invention can have a CTE in the range of 25-40 x 10^{-7}/°C, preferably in the range of 30 to 40 x 10^{-7}/°C

[0007] The invention is further directed to borosilicate glasses and glass frits having a base composition in mole percent (mol %) of:

B_2O_3 = 12 - 22 mol %

SiO_2 = 68 - 80 mol %; and

additional substances selected from the groups of either:

(a) Al_2O_3 = 3 - 8 mol % and Li_2O = 1 - 8 mol %, or

(b) K_2O = 0 - 2 mol % and Na_2O = 0 - 2 mol %, except that both K_2O and Na_2O cannot both equal zero at the same time.

In addition, one or more of calcium oxide (CaO) in an amount of 1.0 - 1.4 mol %, zirconium oxide (ZrO_2) in an amount of 0.5 ± 0.1 mol %, fluorine (F) in an amount less than 1.5 mol%, and sodium oxide (Na_2O) in an amount less than 3 mol% can optionally be added to combination of the glass of the base composition and (a) as above.

[0008] The invention is also directed to borosilicate glasses and glass frits having a composition in mole percent (mol%) of B_2O_3 = 18 - 22 mol %, SiO_2 = 75 - 80 mol %, K_2O = 0 - 2 mol %, and Na_2O = 0 - 2 mol %, except that both K_2O and Na_2O cannot both equal zero at the same time.

[0009] Additionally, the invention is directed to glasses, and frits made therefrom, having the following compositions:

1. SiO_2 = 72.6 ± 0.5 mol%, B_2O_3 = 13.4 ± 0.5 mol% , Al_2O_3 = 6.5 ± 0.4 mol%, Li_2O = 6.9 ± 0.4 mol%, and ZrO_2 = 0.5 ± 0.1 mol%.
2. SiO_2 = 70.2 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol% , Al_2O_3 = 3.4 ± 0.4 mol%, Li_2O = 1.4 ± 0.2 mol%, Na_2O = 2.3 ± 0.2 mol%, CaO = 1.1 ± 0.2 mol% and F = 1.1 ± 0.2 mol%.
3. SiO_2 = 78.1 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 1.5 ± 0.2 mol%.
4. SiO_2 = 78.0 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 0 - 1.0 ± 0.2 mol% and Na_2O = 0.8 - 1.6 ± 0.2 mol%.
5. SiO_2 = 78.0 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 0.4 ± 0.2 mol% and Na_2O = 1.2 ± 0.2 mol%; and
6. SiO_2 = 78.0 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 0 mol% and Na_2O = 1.6 ± 0.2 mol%.

[0010] The glass compositions according to the invention that are suitable for frit use have a crystallized depth layer, as measured by the HTS method described herein using bulk glass, of less than 30 μm as measured after sintering on frit bars, preferably less than 20 μm, and most preferable 10 μm or less. Further, the glass compositions have a softening point less than 825 °C, preferably less than 800 °C, and CTE $< 35 \times 10^{-7}$/°C.

Brief Description of the Drawings

[0011] Figure 1 is a top view of a microreactor having a T-shaped reaction structure microreactor that has been etched into a substrate.

[0012] Figure 2 is a side view of the microreactor of Figure 1 that further illustrates the placement of a top plate over the substrate having the reactor structure etched therein.

[0013] Figure 3 illustrates a process for making a microreactor, in this illustration the microreactor being a multi-level complex design.

[0014] Figure 4 is a side view of a microreactor illustrating a bottom substrate, a frit with the microreactor design therein as represented by the horizontal lines and a top substrate having at least openings for the entry and exit of fluids.

[0015] Figure 5 is a microphotograph of a $B_2O_3/Al_2O_3/Li_2O/SiO_2$ glass frit according to the invention illustrating that the frits according to the invention do not crystallize even when alumina particles are present as a result of steps such as cutting and grinding using alumina saws and grinding devices.

[0016] Figure 6 is a microphotograph illustrating the crystals found in a composition containing fluorine and the oxides of sodium, lithium, aluminum, calcium, boron and silicon.

[0017] Figure 7 is a microphotograph illustrating a composition not of the invention containing alumina and lithium that contains an amount of stuffed β-quartz crystals after sintering.

[0018] Figure 8 is a microphotograph of a glass composition according to the invention that shows no crystallization after sintering.

[0019] Figure 9 is an illustration of the thermal expansion dynamic mismatch curves for composition 723 CWF frit layers in slight tension or compression.

[0020] Figure 10 illustrates of the mismatch in the butt seal using a BM 5 composition frit and Eagle 2000 substrate following 680 °C presintering and 800 °C sintering.

[0021] Figure 11 illustrates butt seal mismatch for composition BM 5-721UP on Eagle 2000 substrate.

[0022] Figure 12 illustrates butt seal mismatch for composition BM 5-721UP on Eagle 2000 substrate, presintered and sintered cooling data with 1 hour 38 minute hold at 526 °C and a cooling rate of 4 °C/minute.

[0023 Figure 13 illustrates thermal expansion mismatch versus time for a BM 5-721UP frit on Eagle 2000 substrate (presintered and sintered) during a hold at 526 °C.

[0024] Figure 14 illustrates butt seal mismatch for BM 5-721UP, Blend 6500 and Blend 6513 frits on Eagle 2000 substrate after presintering and sintering.

Detailed Description of the Invention

[0025] A process for the manufacturing of microreactors can be based on micro-molding of glass frit structures onto a substrate and then covering the frit with an appropriate cover layer of material. This process is based on the micro-molding techniques disclosed in U.S.

Patent No. 5,853,446 (the ‘446 patent) that are used to make formed glass structures that are particularly useful for forming barrier rib structures for use in plasma display units.

[0026] Figure 2 of the ‘446 patent illustrates a frit bonded (adhered) to the substrate. To make a microreactor, two substrates (first or bottom and second or top substrates) would be used and the frit would be sandwiched between them as illustrated in Figure 4 of this application.

[0027] One process for making a microreactor uses two firing steps to consolidate frit structures. The first firing step or heat treatment, called “pre-sintering”, is made at a temperature at which the viscosity of the frit is approximately 1×10^{10} poise and for a time in the range of 25-40 minutes to ensure initial densification of the frits glass composition. This first heat treatment is needed to achieve sufficient frit structure strength and to provide adequate adhesion of the frit layer to a substrate prior to any further processing or machining (for example: dicing, drilling, polishing, etching or other processing steps). Once the additional processing steps have been completed, a second firing or heat treatment step (also called the sintering or curing cycle) is needed to seal the stacked layers and the frit and the substrate together, complete full densification and achieve gas tightness of the frit structures. This final curing is made at a frit viscosity of approximately 1×10^{7} poise for a time in the range 20-45 minutes.

[0028] Figure 3 illustrates, in a very general way, a molding process for making a microreactor, in this case a microreactor having a complex, multi-layer design. Box 100 represents the mask design and production of the master mold which is used to make a production mold 120 out of a material such as a silicone. A suitable substrate 110 is selected and the frit composition 112 is placed on substrate 110. The mold 120 is then applied to the composition 114 on substrate 110 to form the frit design as indicated at 126; and after removal of the mold the composition is pre-sintered as described above. A top substrate 128 is placed over the frit/substrate combination represented by 126 and appropriate openings are drilled as indicated by numeral 140. Several layers of frits can be combined and then cured together to form the finished microreactor 130. Figure 4 represents a very simple microreactor such as the T-shaped microreactor illustrated in Figure 1. The microreactor 200 is comprised of a bottom substrate 210, a molded frit 220 with the reactor design therein as represented by 230 and top substrate 240 that has openings 250 therethrough for the entry and exit of fluids. The substrate glasses are commercially available borosilicate and boroaluminosilicate glasses such as Corning 7740, 1737, 7761 and Eagle 2000 glasses, all of which are commercially available.

[0029] U.S. Patent Application Publication 2004/0152580, published August 5, 2004 (the '580 publication), commonly owned with this application by Corning Incorporated, describes borosilicate frits that are resistant to crystallization of polymorph silica crystals and also compatible with the microreactor process. However, these frits partially crystallized (approximately 5-10% stuffed beta quartz crystals) after the two-step firing process described above. The present invention relates to improved borosilicate frits having a coefficient of thermal expansion matched with a similar viscosity to glasses reported in the '580 publication, but has higher resistance to crystallization than the frit compositions described in the '580 publication. Frits of the present invention are made from glass compositions that have a crystallized depth layer, as measured by the HTS method described herein using bulk glass, of less than 30 μm as measured after sintering on frit bars, preferably less than 20 μm, and most preferable 10 μm or less.

[0030] In accordance with the invention, in making the microreactors it is preferred that the glass substrate be made of a low thermal expansion glass, preferably one having a thermal expansion in the range of 25 to 40 x 10^{-7}/°C, preferably in the range of 30 to 40 x 10^{-7}/°C. Accordingly, in accordance with the invention the material used to make the frit should be made of a low thermal expansion material; should also have a softening point temperature that does not exceed 850 °C, and preferably less than 800 °C, in order to prevent deformation (creping) of the substrate 1737 or Eagle 2000 during firing; should have high crystallization resistance in order to insure full densification and good strength; and should have a high chemical resistance to acids and alkalies (the higher the better). The frit compositions according to the invention satisfy these criteria.

[0031] The borosilicate glass frits of the present invention have a base composition in mole percent (mol %) of:

B_2O_3 = 12 - 22 mol %

SiO_2 = 68 - 80 mol %; and

and as additional substances either:

(a) Al_2O_3 = 3 - 8 mol % and Li_2O = 1 - 8 mol %, or

(b) K_2O = 0 - 2 mol % and Na_2O = 0 - 2 mol %, except that both K_2O and Na_2O cannot both equal zero at the same time.

In addition, one or more of calcium oxide (CaO) in an amount of 1.0 - 1.4 mol %, zirconium oxide ZrO_2) in an amount of 0.5 ± 0.1 mol %, fluorine (F) in an amount less than 1.5 mol%, and sodium oxide (Na_2O) in an amount less than 3 mol% can optionally be added to the a glass of the base composition and (a) as above (the amounts of the other components being adjusted accordingly).

[0032] Borosilicate glasses and glass frits according to the invention can also have a composition in mole percent (mol%) of B_2O_3 = 18 - 22 mol %, SiO_2 = 75 - 80 mol %, K_2O = 0 - 2 mol %, and Na_2O = 0 - 2 mol %, except that both K_2O and Na_2O cannot both equal zero at the same time.

[0033] Examples of some of the preferred glass compositions for the 1737 substrate, and similar substrates known to those skilled in the art, are:

1. SiO_2 = 72.6 ± 0.5 mol%, B_2O_3 = 13.4 ± 0.5 mol% , Al_2O_3 = 6.5 ± 0.4 mol%, Li_2O = 6.9 ± 0.4 mol%, and ZrO_2 = 0.5 ± 0.1 mol%.
2. SiO_2 = 70.2 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol% , Al_2O_3 = 3.4 ± 0.4 mol%, Li_2O = 1.4 ± 0.2 mol%, Na_2O = 2.3 ± 0.2 mol%, CaO = 1.1 ± 0.2 mol% and F = 1.1 ± 0.2 mol%.
3. SiO_2 = 78.1 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 1.5 ± 0.2 mol%.

Further, the glass compositions suitable for frit use have a crystallized layer depth, as measured on bulk glass using the HTS method described herein, of 30 µm or less, preferably 20 µm or less, and most preferably 10 µm or less.

[0034] Preferred glass compositions for the Eagle2000 substrate, and similar substrates known to those skilled in the art, have a composition in mole percent (mol%) of B_2O_3 = 18 - 22 mol %, SiO_2 = 75 - 80 mol %, K_2O = 0 - 2 mol %, and Na_2O = 0 - 2 mol %, except that both K_2O and Na_2O cannot both equal zero at the same time. A preferred composition is:

4. SiO_2 = 78.0 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 0 - 1.0 ± 0.2 mol% and Na_2O = 0.8 - 1.6 ± 0.2 mol%.

Especially preferred compositions are:

5. SiO_2 = 78.0 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 0.4 ± 0.2 mol% and Na_2O = 1.2 ± 0.2 mol%; and
6. SiO_2 = 78.0 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 0 mol% and Na_2O = 1.6 ± 0.2 mol%.

The foregoing glass compositions suitable for frit use have, after heat treatment, a crystallized layer depth of 30 μm or less, preferably 20 μm or less, and most preferably 10 μm or less.

[0035] Borosilicate glass powders described in the present invention were prepared from quartz, anhydrous boric oxide, boric acid, calcined alumina, alkali carbonates and, optionally, alkaline-earth carbonates. After mixing, the vitrifiable mixture was melted in an induction furnace at 1650 °C for 6 hours in a platinum-rhodium crucible. The melted glasses were then quenched in water and milled under dry conditions using an alumina ball mill. The ball-milled powder was then sieved (to < 63 μm) and paste samples were prepared from the sieved powder mixed with wax material (for example, MX4462) by molding a flat layer onto a selected substrate; for example, a Corning 1737 or Eagle 2000 glass substrate. The samples were then heated (pre -sintered and sintered) according to the two-step process described above.

[0036] The crystalline phases present in samples were identified and analyzed by both x-ray diffraction ("XRD") and scanning electron microscope ("SEM") analysis. XRD helps to identify the nature and determine the amount of crystalline phase whereas SEM observations inform on dimensions, shapes and localization of the crystals among residual glass. In addition, a specific test designated "HTS" herein was used to evaluate the crystallization resistance of "bulk" glasses by heat treating a polished piece of glass (for example, a bulk glass obtained from the crucible melt described in the previous paragraph, or cored/sawed from a large boule) for forty-eight (48) hours at the glass' softening point temperature (typically corresponding to a viscosity in the range of 10^7 to 10^8 poise for the glasses described herein). The extent of crystallization was compared from one composition to another by measuring the thickness of the crystallized layer and the dimensions of the crystals. The lower the HTS value the greater the crystallization resistance of the glass. HTS values of 30 μm or less are preferred, with values less than 20 μm being especially preferred. A glass having a HTS value of approximately 10 μm or less is deemed to be totally amorphous when used in powder form after the two-step firing process. The polishing of the glass piece used for the HTS test was carried out using cerium oxide and standard glass polishing methods known in the art, for example, methods described or referenced in the *Handbook of Ceramic Grinding and Polishing*, eds. I.M. Marinescu et al (Park Ridge, NJ USA, Noyes Publications 2000), pp. 374-389.

[0037] The thermal expansion of the frits was measured by thermal mechanical analysis ("TMA") or by dilatometry. Glasses according to the invention have a coefficient of thermal expansion (CTE), measured as bulk glass, in the range of 25-40 x 10^{-7}/°C. The CTE value should be smaller than that of the substrate glass in order to avoid tensile stresses building up during use and fracturing the reactor. The glasses of the invention also have a softening point less than 800 °C. As a general rule, the softening point of the frit glass should be less than that of the substrate. Consequently, some adjustment of the glass composition may be necessary if the substrate glass is changed. Seal stresses were examined via polarimetric techniques and mismatch as a function of temperature also recorded. Glass viscosity between 10^8 to 10^{13} poise was measured by the fiber elongation method for bulk glasses. Chemical durability was determined by measuring the weight loss of samples immersed in acid or alkaline media in accordance with DIN 12116 (acid), and ISO 695 (alkali).

[0038] Alumina in a borosilicate glass composition inhibits, and may even prevent, the formation of polymorph silica crystals in alkali borosilicate frits. However, when a substantial quantity of alumina is added into the glass composition the softening point temperature of the glass, or a glass frit made with the composition, increases drastically. Consequently, in order to maintain a low softening point and to satisfy maximum processing temperature requirements, it is necessary to add flux components, or to increase the amount of the flux components if they are already present, to balance the alumina effect. Since a strong coupling occurs in glass networks between Li+ and Al3+, Li_2O was selected as the flux material to soften the glass. A borosilicate glass composition designated in Table 1 as REAC 66 was found to have good crystallization resistance and very good chemical resistance. This glass composition contains Al_2O_3 and Li_2O. However, even if crystallization of polymorph silica crystals is actually inhibited by alumina, there is always a concern that when alumina and lithium are present together in a frit composition, a minor amount of stuffed β-quartz crystals will frequently still occur during sintering (see Figure 6, Sample REAC 70).

[0039] The invention has resulted in new alkali borosilicate frits which are more resistant to crystallization than prior compositions. The sintered structures made with these frits remained totally amorphous after the two-firing step process. The new frits do not crystallize during sintering even if particles such as alumina particles (see Figure 5) coming from grinding or others impurities are present into the paste before sintering. This great level of crystallization resistance is achieved by increasing the boron content of the glass frit composition. For example, the glasses designate BM 5 and 723 CWF bulk glass exhibit only a small amount of crystallization after the long duration heat treatment of the HTS test. For each of these samples a crystallized layer depth measured from the top surface is only 10μm versus, for example, 226 μm for 7740 glass processed under similar conditions. [See Figure 7 for a microphotograph of the crystallized layer for the 7740 glass]. While the 7761 glass has a high crystallization resistance, it also has a high softening point which is undesirable for matching 1737 or Eagle2000. Consequently, a lower softening point glass having the high crystallization resistance of the 7761 glass was discovered as disclosed herein. [As a result, the crystallization of the 7740 glass illustrated in Figure 7 is avoided.] In addition, when a layer of glass frits made from the BM 5 or the 723 CWF compositions was sintered, the frit remained completely amorphous. No crystals (either cristobalite or stuffed quartz phase such as β-eucryptite) were observed as is shown in Figure 8 for the 723 CFW composition. Thus, for these frits, both crystal families [silica polymorphs such as cristobalite, α-quartz, tridymite or stuffed β-quartz such as β-eucryptite] are inhibited by boron. In addition, the study has confirmed that alkalies enhance cristobalite tendency to crystallize and that low alkali content will further eliminate crystallization. As an example of the need for boron to reduce the tendency to crystallize compare compositions BM 3, BM 4 and BM 5 in Table 2. Sample BM 5 has an analyzed K_2O content of 1.5 mol% and a crystallized depth of 10 μm. In contrast, BM 3 and BM 4 have analyzed K_2O contents of 3.5 and 4.2 mol%, respectively, and crystallized depths of 38 and 70 μm, respectively. The comparison illustrates the tendency for a crystallized layer to form with increasing alkali content when an inhibitor such as boron is not included.

[0040] The glass compositions according to the invention have very good level of acid resistance, their acid resistance as determined by DIN 12116 (see Tables 1 and 2) being similar to 7740 glass which is a Pyrex® glass used to make laboratory glassware (see values for BM 5 and BM 7). However, by increasing boron content above 13% (mol), there is some lowering of the alkali resistance (ISO 695 values in Tables 1 and 2)) of the glasses. Values for alkali tests increase from 102 mg/dm2 (7740 glass) to values of 374 and 1220 for the BM 5 and 723 CWF compositions, respectively.

[0041] Regarding mismatch for a frit coating applied to a substrate, the magnitude and sign of seal stress can be managed over a large temperature range by adjusting the thermal cycle on cooling step that occurs after the final assembly. For example, on code 1737 glass substrate, all frit layers of 723 CWF are typically in slight tension after cooling as shown in thermal expansion dynamic mismatch curves (see Figure 9). It is also possible to design a cooling schedule containing an annealing hold period which will place the 723 CWF frit into mild compression. This imparts a real advantage to the compositions of the invention because one can reach compression or tension for the frit structures with a single composition.

[0042] The glass compositions according to the invention impart an advantage over previously known borosilicate glass frits by providing new families of borosilicate frits that have similar properties of thermal expansion, chemical stability and viscosity as Pyrex® 7740 or 7761 frit glasses, and additionally have a very strong crystallization resistance not found in glass frits made from 7740 glass. The new frits according to the invention did not crystallize during the two-firing steps as used in conducting the experiments reported herein in spite of the presence of impurities that may be present in the paste. The glass frit compositions according to the invention can form hermetic sintered channels on glass substrates in accordance with the process described in US Patent 5,853,446 (3). The microreactor channels formed in the frits are vitreous, translucent, chemically durable and resistant to thermal shock. The frits can also be matched to different substrate materials, for example a 1737 or Eagle2000 substrate, over a large temperature range (300°C), and the sign and magnitude of mismatch can be tailored by the thermal cycle.

[0043] Tables 1 and 2 describe a number of glass compositions that were prepared and evaluated for use as frits. Compositions REAC 66, 720 CWF and BM 5 were found to most closely match frit requirement for substrates made of 1737 glass which is commercially available from Corning Incorporated. Other glass compositions that can be used are the REAC 70 and REAC 82 which have a crystalline layer less than 20 µm. All glass composition according to the invention have a CTE close matched to substrate CTE values and also have softening points that are below that of the substrate and are below 825 °C to ensure that the glass can be properly sealed to the substrate without requiring high temperatures that may induce the composition to form crystals or deform the substrate. All compositions shown in Tables 1 and 2 are by analysis of a specific batch and can vary from batch to batch. The preferred compositions REAC 66, 723 CWF and BM 5 have values that fall within the ranges given on page 5 of this specification.

Table 1

% mol	7740	REAC 66	REAC 70	REAC 82	723 CWF	720 CWF
SiO_2	83.3	72.6	73	73.8	70.2	69.7
B_2O_3	11.5	13.4	13.4	15.5	20.4	20.8
Al_2O^3	1.2	6.5	6.1	4.9	3.4	3.4
Li_2O		6.9	6.8	4.2	1.4	1.4
Na_2O	4			1.6	2.3	2.3
ZnO			0.8			
CaO					1.1	1.1
ZrO_2		0.5				
F					1.3	1.3
Bulk glass CTE (10-7/°C)	32.5	33.6	36.4	35.3	34.8	36.7
Softening point (°C)	825	819	780	779	757	734
HTS: crystalline phases (XRD)	crist.	amorph.	B-quartz	B-quartz	amorph.	B-quartz crist.
HTS : crystallized layer depth (µm)	226		10	10		nm
DIN 12116 (mg / dm2)	< 0.1	4.8	9.2	8.4	50	
ISO 695 (mg / dm2)	102	112	222	239	1220	

crist. = cristobalite
amorph. = amorphous
1737 is a Corning Pyrex® glass formulation with excellent acid and alkali resistance

Table 2

% mol	7761	BM 3	BM 4	BM 5	BM 6	BM 7
SiO_2	82.1	79.9	79.2	78.1	76.4	74.5
B_2O_3	16.4	16.6	16.7	20.4	22.1	23.9
K_2O	1.5	3.5	4.2	1.5	1.5	1.5
Bulk glass CTE (x10-7/°C)	26.8	31.7	37.4	30	31.6	32.3
Softening point (°C)	842	788	782	783	764	758
HTS: crystalline phase (XRD)	crist.	crist.	crist.	crist.	crist.	crist.
HTS : crystallized layer depth (μm)	not measured	38	70	10	not measured	not measured
DIN 12116 (mg / dm2)	0.15			< 0.1		0.7
ISO 695 (mg / dm2)	376			374		568

crist. = cristobalite
amorph = amorphous
7761 is a Corning Pyrex® glass formulation with excellent acid and alkali resistance.

[0044] A preferred substrate for microreactor devices is Corning's commercially available Eagle 2000 glass. Because the glass frits defining the microreactor structure seal directly to the substrate, CTE compatibility between the substrate and the frit is a major concern. The CTE of the Eagle 2000 glass is in the range of 30-32 x 10^{-7}/°C. While, as indicated above in Experiment 1, the 7761 and 7740 glasses could be used as frit materials, they are not ideal for the Eagle 2000 substrate because either the softening point is too high or because they fail the crystallization test. Ideally, the softening point should be less than 800 °C, preferable less than approximately 780 °C, and the crystallized layer should be less than 30 μm and preferably 10 μm or less. The BM 5 glass shown above in Table 2 meets both these criteria. As a result, a series of experiments was performed to optimize the BM 5 composition for use with the Eagle 2000 substrate. This was carried out by replacing K_2O with Na_2O in the composition. Table 3 gives the results of these experiments. BM 5 - 721UP is the same composition as BM 5 in Table 2.

Table 3. Effect of Replacing K with Na in BM-5 Glass

(mole %)	BM 5-721UP	BM 5-721UQ	BM 5-721UR	BM 5-721US	BM 5-721UT
SiO_2	78.0	78.0	78.0	78.0	78.0
B_2O_3	20.4	20.4	20.4	20.4	20.4
K_2O	1.6	1.2	0.8	0.4	---
Na_2O	---	0.4	0.8	1.2	1.6
Bulk glass CTE (10^{-7}/°C)	32.3	30.1	28.9	28.6	27.0
RT mismatch, 1737 butt seal sintered at 800°/1hr (ppm)	-41	-56	-70	-92	-104
Softening pt	783				772°
HTS crystallization layer depth (μm)	10				10
DIN 12116	< 0.1				<0.1
ISO 695	374				342

* DIN 12116 - 6 hr. boiling in 6N HCl
** ISO 695 - 3 hr. boiling in 1N NaOH/Na_2CO_3
Missing values for BM 5 -712UQ, -721UR and -721US are the same as or transitional between the values for BM 5 -721UP and BM 5 -721UT

[0045] To evaluate the expansion compatibility between frit candidates and Eagle 2000 glass, extensive use was made of photoelastic measurements to evaluate residual and transient strains arising from CTE mismatch. Model seals of frit and the Eagle 2000 substrate were prepared and evaluated. These seals were typically butt seals where the frit was applied to one surface of the substrate (typically, a 10x10x20mm substrate) to mimic a microreactor. The seal was prepared using a paste of amyl acetate and nitrocellulose as the vehicle/binder system, and then fired in a furnace on the desired presintering and sintering schedules used for microreactor fabrication as is described above. Following firing, the residual mismatch in the frit was measured at room temperature. Alternatively, an already-fired specimen was heated to a temperature at which all stresses were relieved, and then transient mismatch was measured in the seal as it was cooled down. Both room temperature and transient mismatch values were obtained with a polarimeter to measure optical retardation. The photoelastic measurements were used to calculate the total expansion mismatch, δ_T, between the substrate glass and the frit according to the equation:

$$\delta_T = \Delta T(\alpha_g - \alpha_f)$$

where: α_g, α_f = expansion coefficients of glass, and frit, respectively; and

ΔT = temperature range of interest

References with regard to the calculations are; [1] H.E. Hagy, "A Review and Recent Developments of Photoelastic Techniques for the Measurement of Thermal Expansion Differentials using Glass Seals, " Proceeding of the Thirteenth International Thermal Expansion Symposium, Technomic Publishing Co., pp. 279-290 (1999); and [2] ASTM Designation F140-98, "*Standard Practice for Making Reference Glass-Metal Butt Seals and Testing for Expansion Characteristics by Polarimetric Methods,*" Annual Book of ASTM Standards 2002, vol. 15.02, pp. 514-519. (Note: Although this ASTM practice is written for glass-metal seals, it is perfectly adaptable for frit-glass seals).

[0046] Figure 10 shows expansion mismatch data obtained on a butt seal sample of BM-5 frit (melted as 721UJ), and Eagle 2000 glass. The butt seal sample was first fired to 680 °C for presintering, re-heated in a different furnace (one equipped with a polarimeter) to approximately 580 °C to relieve all mismatch strains, and then cooled slowly to monitor the re-appearance of the mismatch strains. Following this, the sample was then heated to 800 °C for sintering, and then re-heated in the polarimeter furnace as per the above procedure, so that mismatch strains corresponding to the sintering schedule could be measured during cooling. After each run in the polarimeter furnace, room temperature mismatch measurements were taken to assure that the residual strain after the presintering or sintering schedule was restored following the thermal cycle in the polarimeter furnace. The mismatch values shown in Figure 10 (in ppm) correspond to those in the substrate glass at the frit-substrate interface. As such, mismatch values >0 (i.e., positive) denote that the frit is in undesirable tension. (Note that the frit is in tension following both the presintering and sintering schedules). In addition, transient values for the frit measured during the sintering schedule approach 180 ppm, a high strain state, and one not desired for a seal involving brittle materials. Preferred glass composition have mismatch values less than -20 (that is, are more negative than -20), and preferably less than -50

[0047] It is apparent from Figure 10, that BM-5, despite its good expansion compatibility with 1737 seen in Table 2, does not have the best expansion-match to the lower CTE substrate, Eagle 2000. As may be seen in Table 2, BM-5 is a potassium borosilicate glass. Typically, replacement of modifying cations such as potassium in a silicate glass by species of smaller size (but with the same charge) results in a lower CTE, since the higher field strength of the substituting ions produce an overall tightening of the silica tetrahedral framework. Shown in Table 3 above are data pertaining to the progressive molar replacement of K^{+1} by Na^{+1} for 721UP, the starting glass with composition essentially that of BM-5 described in Table 2 (the difference is 0.1 mol for both K_2O and B_2O_3). It should be noted that progressive replacement of K by Na (while maintaining the same B:Si ratio) resulted in a continual decrease in CTE. This is also suggested by the RT mismatch data for butt seals.

[0048] To determine the expansion compatibility of 721UT with Eagle 2000 glass, butt seals were prepared, fired on presintering (680 °C) or presintering (680^o) and sintering (800 °C) schedules, re-heated in the polarimeter furnace to a temperature at which stress was relieved, and then cooled to collect retardation/mismatch data. These data are shown in Figure 11. The improved mismatch of 721UT with Eagle 2000 is compared to that of BM-5 (Figure 10). After presintering, 721UT is in mild compression, unlike BM-5 which was in tension. Following presintering and sintering, 721UT is in very mild tension (approx. +30ppm) versus BM-5 which is in moderate tension (+90ppm). As seen in Table 3, 721UT also possesses the appropriate softening point needed for firing microreactor structures, as well as exhibits excellent crystallization and corrosion resistance.

[0049] Although the mismatch strain levels in 721UT on Eagle 2000 are acceptable, the possibility of achieving additional reductions was explored using several different techniques such as: (a) annealing after 800 °C sintering hold; (b) addition of a filler to lower CTE; and (c) composition iterations around 721UT.

[0050] The effect after annealing after 800 °C sintering hold is illustrated in Figure 12 by the mismatch readings for a 721UT-Eagle 2000 butt seal that was held at 526 °C during the cool-down from the 800 °C sintering hold. Note that, in comparison to Figure 10 the maximum value of transient strain during cooling was reduced by approximately half (from +200ppm to +100ppm), and that the residual (or room temperature) mismatch now shows the frit in desirable compression. The actual relief of the mismatch strains during the annealing hold at 526 °C is shown in Figure 13 for the 721UT-Eagle 2000 butt seal. Note that mismatch strain follows a classic Maxwell-type decay relationship.

[0051] The effect of fillers is to adjust the CTE of the frit to achieve a more acceptable mismatch. We have found that most of the fillers that have been used to lower CTE of the resulting frit mixture (termed “a blend”) have been low CTE compounds obtained through the glass ceramic process. Examples, without limitation, of the materials that can be used as fillers include:

(1) β-eucryptite - a lithia-alumino-silicate composition, with intrinsic CTE = -$10x10^{-7}/^{o}C$;

(2) Stuffed β-quartz - a lithia-alumino-silicate composition, with Zn and/or Mg partially replacing some of the Li; with intrinsic CTE = $0x10^{-7}/^{o}C$; and

(3) β-spodumene - a lithia-alumino-silicate composition, with Zn and/or Mg partially replacing some of the Li; with intrinsic CTE = $+10x10^{-7}/^{o}C$.

Figure 14 illustrates the mismatch data for butt seals to Eagle 2000 following the 800 °C sintering schedule. Shown are 721UT (from Figure 10), and two blends made with BM 5-721UT (simply numbered as 721UT below and in Figure 14) and stuffed Zn-containing β-quartz designated 88MOC. These blends are identified as Blend 6500 (90% 721UT + 10% 88MOC, wt. basis), and Blend 6513 (15% 88MOC or 85% 721UT + 15% 88MOC). Note the progressive improvement of mismatch (i.e., frit becomes progressively in lower tension) with increasing filler addition. Also, it is to be understood that the presence of any of the foregoing fillers in the composition is not to be considered as impacting HTS crystallization depth layer and must be excluded from any determination of the HTS crystallization depth layer.

[0052] The invention can be further considered as being directed to a microreactor having at least the elements of a first substrate, a second substrate and a microreactor frit between the two substrates; where at least one of the top and bottom substrates has an entry opening and/or an exit opening for the entry and exit of the reaction fluids that are passed through the microreactor, and the frit has at least one channel, passageway or path from the entry opening to the exit opening, the frit being made of any glass composition recited herein. Optionally, the microreactor can also have baffles for mixing, heating elements with leads passing through the frit of a substrate, addition openings for the entry of additional substance to the reaction fluids while they travel from the entry opening to the exit opening, sensors with leads, sample ports and other elements such as are known in the art for monitoring, sampling, heating, and cooling. The microreactor can contain a single frit or a plurality of microreactor frits as has been described herein and is illustrated in exemplary manner in Figure 3. Preferred glass compositions include:

1. SiO_2 = 72.6 ± 0.5 mol%, B_2O_3 = 13.4 ± 0.5 mol% , Al_2O_3 = 6.5 ± 0.4 mol%, Li_2O = 6.9 ± 0.4 mol%, and ZrO_2 = 0.5 ± 0.1 mol%.
2. SiO_2 = 70.2 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol% , Al_2O_3 = 3.4 ± 0.4 mol%, Li_2O = 1.4 ± 0.2 mol%, Na_2O = 2.3 ± 0.2 mol%, CaO = 1.1 ± 0.2 mol% and F = 1.1 ± 0.2 mol%.
3. SiO_2 = 78.1 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 1.5 ± 0.2 mol%.
4. SiO_2 = 78.0 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 0 - 1.0 ± 0.2 mol% and Na_2O = 0.8 - 1.6 ± 0.2 mol%.
5. SiO_2 = 78.0 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 0.4 ± 0.2 mol% and Na_2O = 1.2 ± 0.2 mol%; and
6. SiO_2 = 78.0 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 0 mol% and Na_2O = 1.6 ± 0.2 mol%.

[0053] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.

CLAIMS:

1. A borosilicate glass composition suitable for manufacturing microreactor glass frits, said borosilicate glass comprising a base glass composition in mole percent (mol %) of:

B_2O_3 = 12 - 22 mol %
SiO_2 = 68 - 80 mol %, and

additional components selected from the group consisting of:

either:

(a) Al_2O_3 = 3 - 8 mol % and Li_2O = 1 - 8 mol %

or

(b) K_2O = 0 - 2 mol % and Na_2O = 0 - 2 mol %, except that both K_2O and Na_2O cannot both equal zero at the same time;

wherein when said glass composition is the base glass composition and (a), said composition can optionally further comprise one or more substances selected from the group consisting of calcium oxide in an amount of 1.0 - 1.4 mol %, zirconium oxide in an amount of 0.5 ± 0.1 mol %, fluorine (F) in an amount less than 1.5 mol%, and sodium oxide (Na_2O) in an amount less than 3 mol%; and

wherein after sintering a glass frit having said composition has a surface crystalline layer of 30 µm or less, or is amorphous throughout.

2. The glass according to claim 1, wherein said glass comprises:

(i) SiO_2 = 72.6 ± 2 mol%,
B_2O_3 = 13.4 ± 2 mol% ,
Al_2O_3 = 6.5 ± 1 mol%,
Li_2O = 6.9 ± 1 mol%, and
ZrO_2 = 0.5 ± 0.25 mol%; or

(ii) SiO_2 = 70.2 ± 2 mol%,
B_2O_3 = 20.4 ± 2 mol% ,
Al_2O_3 = 3.4 ± 1 mol%,
Li_2O = 1.4 ± 0.8 mol%,
Na_2O = 2.3 ± 0.5 mol%,
CaO = 1.1 ± 0.5 mol% and

$F = 1.1 \pm 0.5$ mol%;

and wherein after sintering in each case said glass frit is amorphous throughout.

3. The glass according to claim 1, wherein said glass comprises:

$SiO_2 = 78.1 \pm 2$ mol%,
$B_2O_3 = 20.4 \pm 2$ mol%, and
$K_2O = 1.6 \pm 0.8$ mol%;

and wherein after sintering said glass frit has a surface crystalline layer of 10 μm or less.

4. A glass according to Claim 1, wherein said glass comprises:

$SiO_2 = 78.0 \pm 0.5$ mol%,
$B_2O_3 = 20.4 \pm 0.5$ mol%,
$K_2O = 0 - 1.2 \pm 0.2$ mol%, and
$Na_2O = 0.4 - 1.2 \pm 0.2$ mol%.

5. A glass composition according to claim 4, wherein said glass comprises:

(i) $SiO_2 = 78.0 \pm 0.5$ mol%,
$B_2O_3 = 20.4 \pm 0.5$ mol%,
$K_2O = 0.4 \pm 0.2$ mol%, and
$Na_2O = 1.2 \pm 0.2$ mol%; or

(ii) $SiO_2 = 78.0 \pm 0.5$ mol%,
$B_2O_3 = 20.4 \pm 0.5$ mol%,
$K_2O = 0$ mol%, and
$Na_2O = 1.0 \pm 0.2$ mol%.

6. The glass according to any of claims 1 to 5, wherein said glass has a softening point of 825 °C or less.

7. The glass according to any of claims 1 to 5, wherein said glass has a softening point of 800 °C or less.

8. The glass according to any of claims 1 to 5, wherein said glass has a softening point of 780 °C or less.

9. The glass according to any of claims 1 to 8, wherein said glass has a CTE in the range of 25 - 40 x 10^{-7}/°C.

10. The glass according to claim 4 or 5, wherein said glass has a CTE in the range of 25 - 35 x 10^{-7}/°C.

11. The glass according to any one of claims 1-10, wherein in a sintered glass frit the mismatch value of said frit with a substrate is less than -20 ppm.

12. A borosilicate glass frit having a composition in mole percent (mol%) of B_2O_3 = 18 - 22 mol %, SiO_2 = 75 - 80 mol %, K_2O = 0 - 2 mol %, and Na_2O = 0 - 2 mol %, except that both K_2O and Na_2O cannot both equal zero at the same time.

13. The borosilicate glass frit according to claim 12, wherein said glass frit has a softening point less than 800 °C.

14. The borosilicate glass frit according to claim 12 or 13, wherein said glass frit has a CTE in the range of 25-35 x 10^{-7}/°C.

15. The borosilicate glass frit according to any of claims 12 to 14, wherein after sintering said sintered glass frit has a crystallization layer of 10 μm or less.

16. The borosilicate glass frit according to any of claims 12 to 16, wherein said glass frit comprises SiO_2 = 78.0 ± 0.5 mol%, B_2O_3 = 20.4 ± 0.5 mol%, K_2O = 0 – 1.2 ± 0.2 mol%, and Na_2O = 0.4 - 1.2 ± 0.2 mol%.

17. The borosilicate glass frit according to any of claims 12 to 16, wherein said glass frit further comprises a filler selected from the group consisting of:

(a) β-eucryptite, a lithia-alumino-silicate composition with an intrinsic CTE of $-10x10^{-7}/^{o}C$;

(b) Stuffed β-quartz, a lithia-alumino-silicate composition with Zn and/or Mg partially replacing some of the Li and that has an intrinsic CTE = $0x10^{-7}/^{o}C$; and

(c) β-spodumene, a lithia-alumino-silicate composition with Zn and/or Mg partially replacing some of the Li and that has an intrinsic CTE = $+10x10^{-7}/^{o}C$.

18. The borosilicate glass frit according to any one of claims 12-17, wherein the mismatch value of said frit with a substrate is less than -20 ppm.

Figure 1
(Prior art)

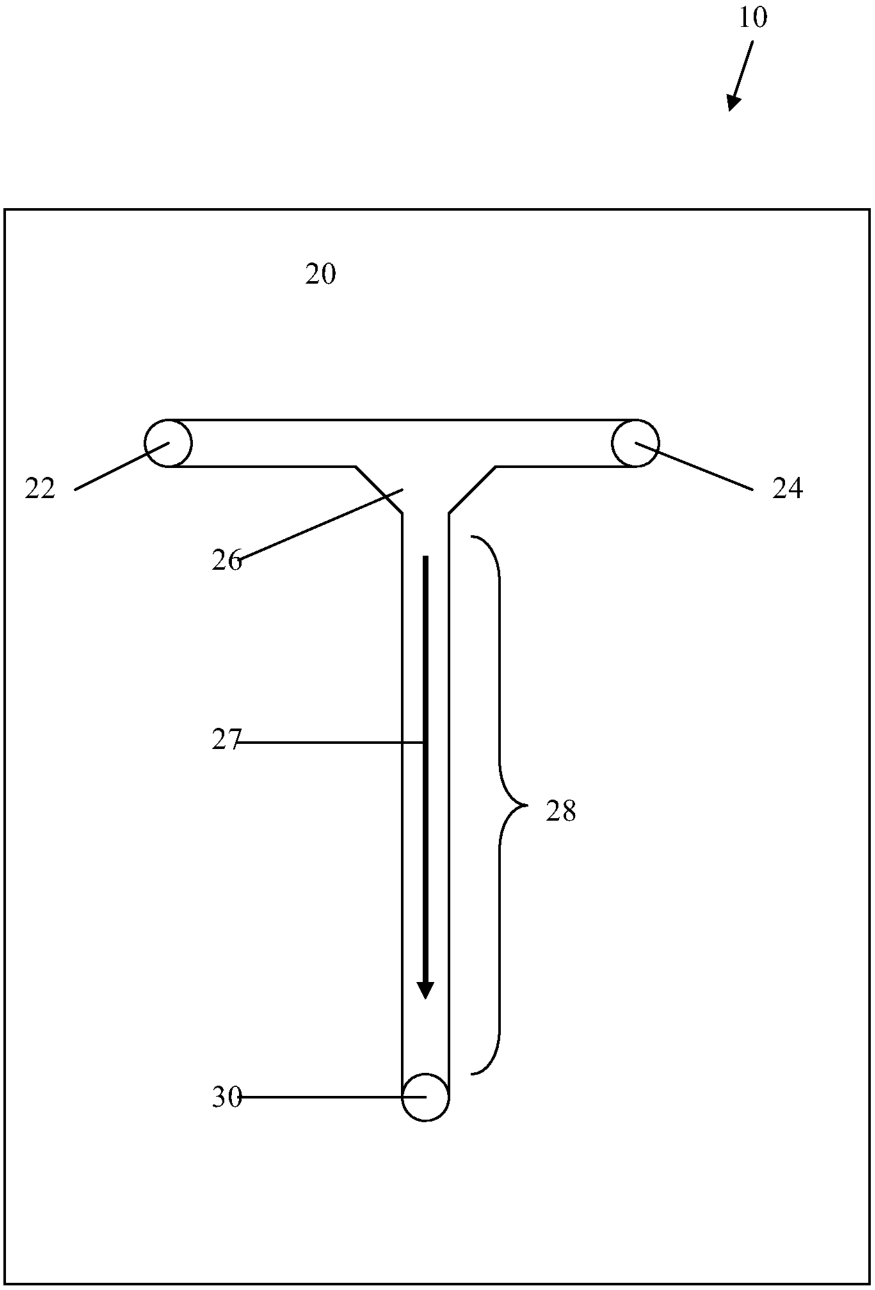


Figure 2

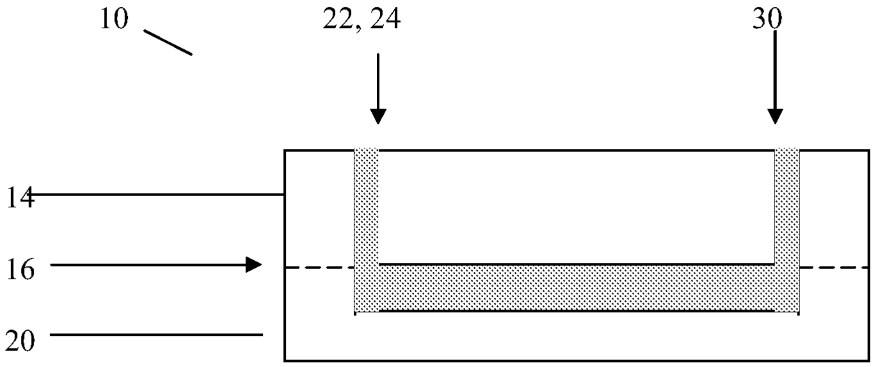


Figure 3

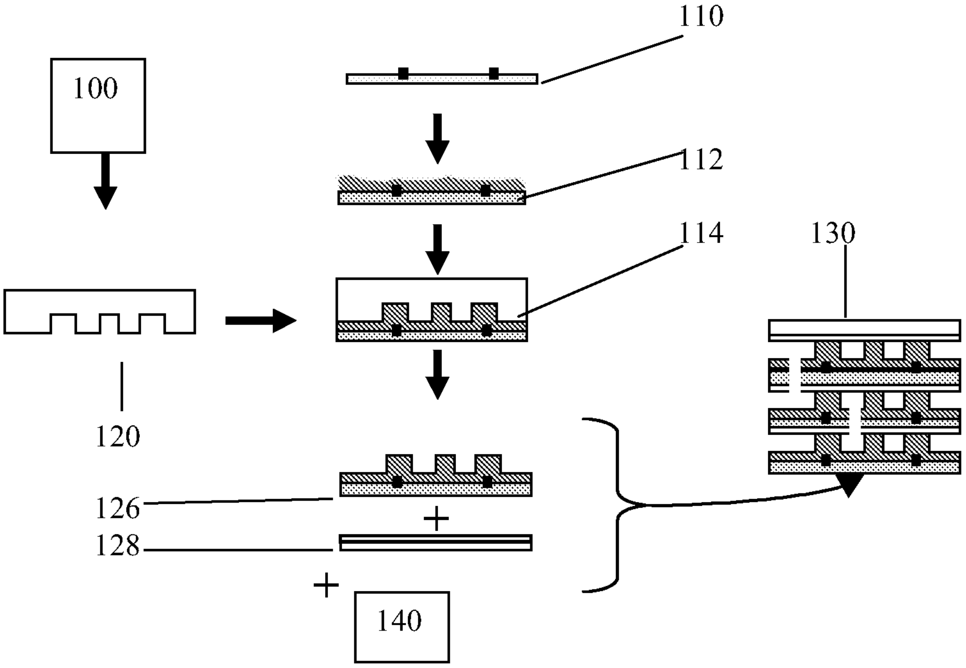


Figure 4

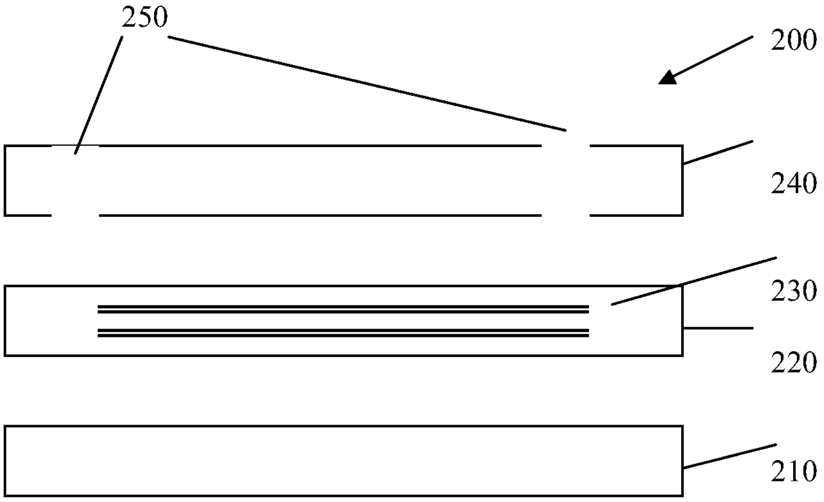


Figure 5

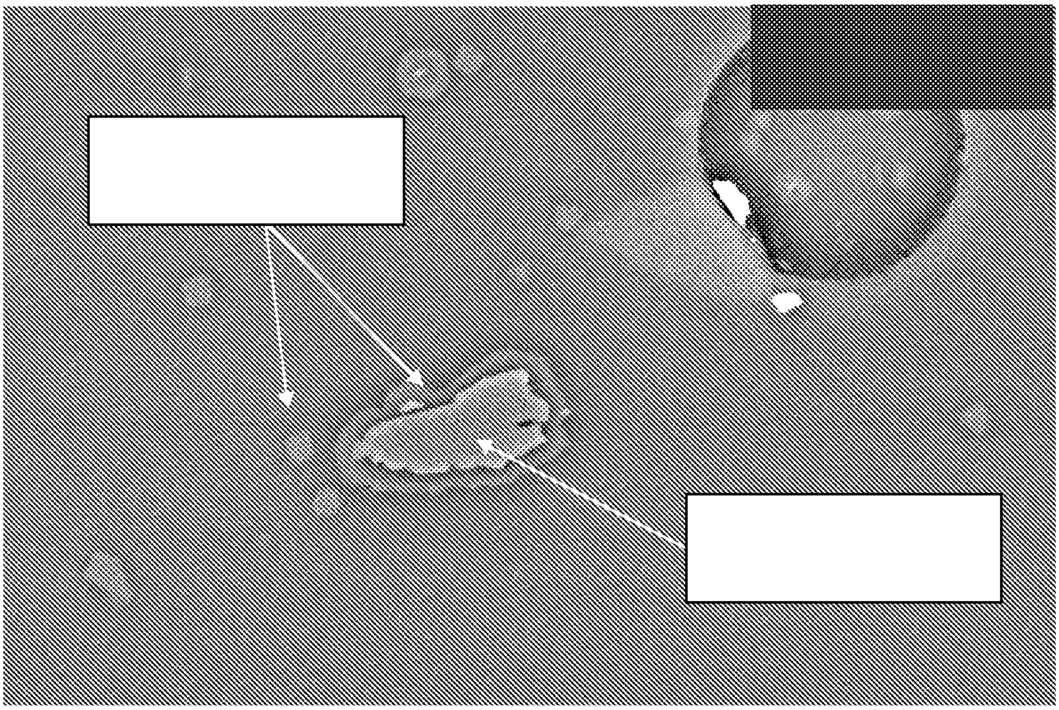


Figure 6

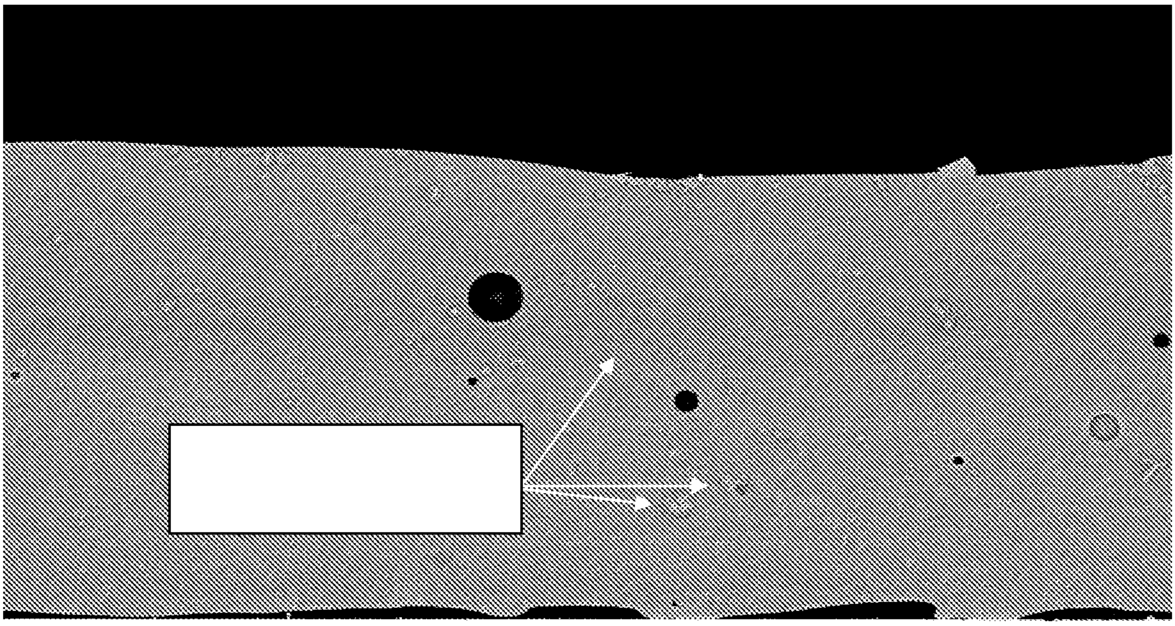


Figure 7

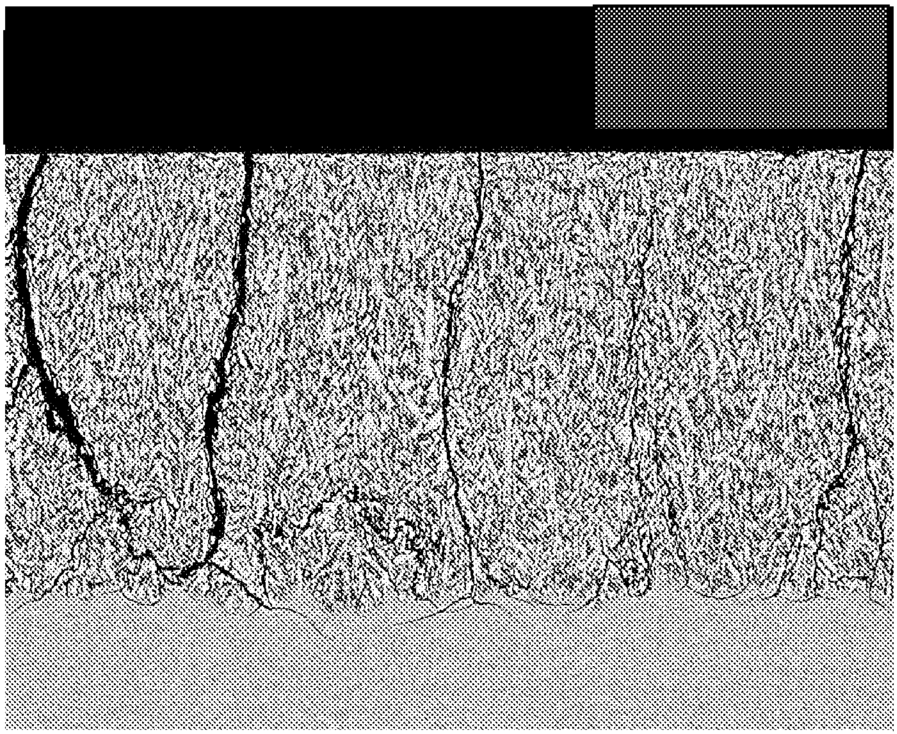


Figure 8

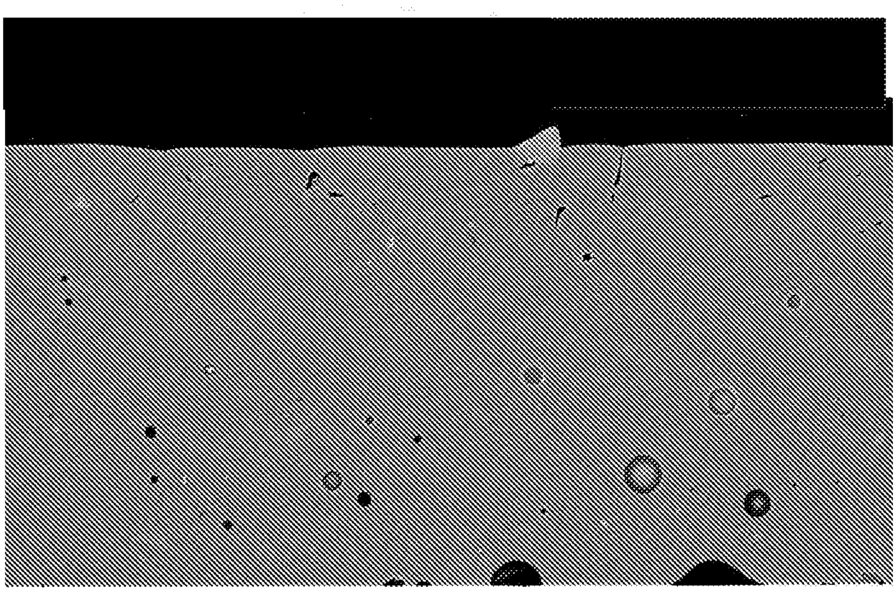


Figure 9

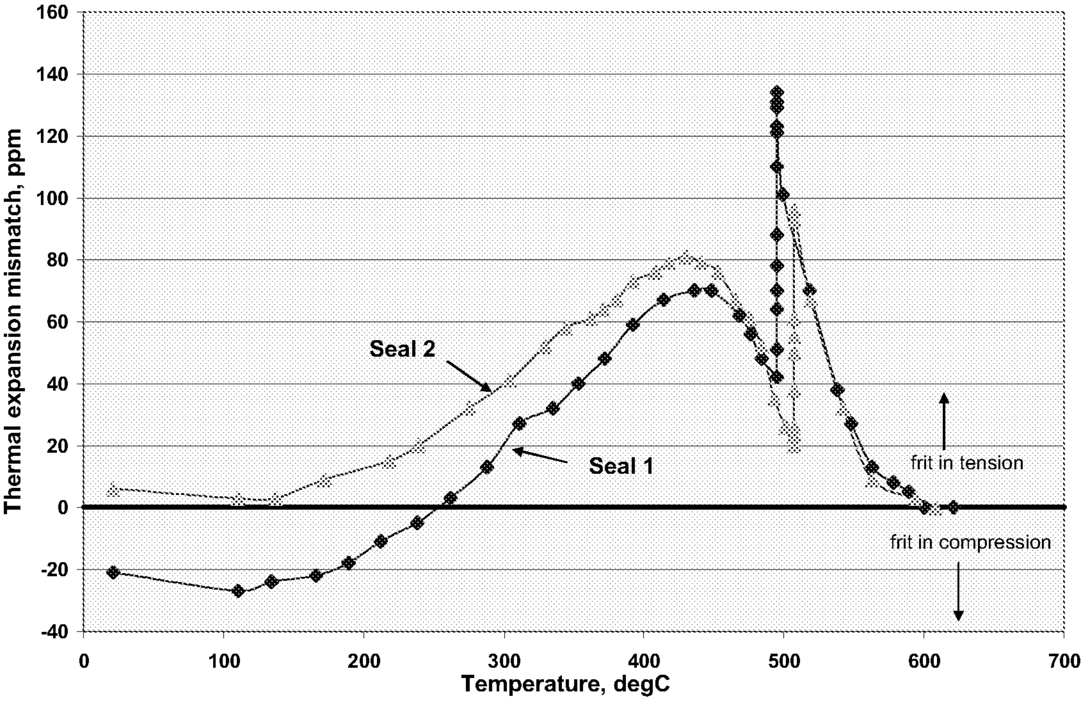

Thermal expansion mismatch, ppm
160
140
120
100
80
60
40
20
0
-20
-40
Seal 2
Seal 1
frit in tension
frit in compression
0
100
200
300
400
500
600
700
Temperature, degC

Figure 10

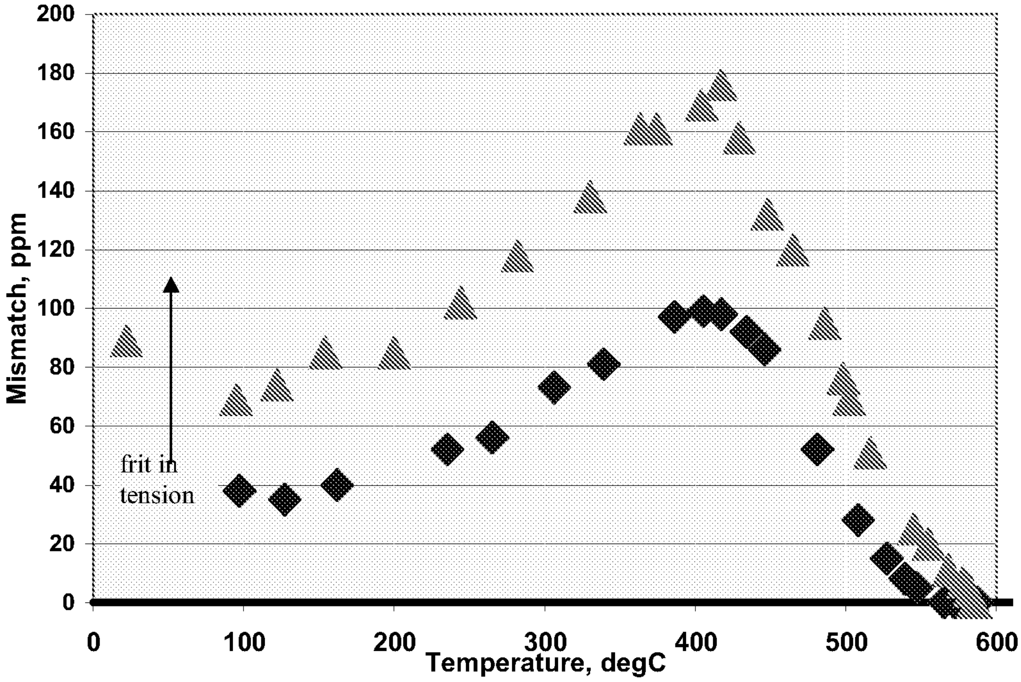

200
180
160
140
120
100
80
60
40
20
0
Mismatch, ppm
frit in
tension
0
100
200
300
400
500
600
Temperature, degC

Figure 11

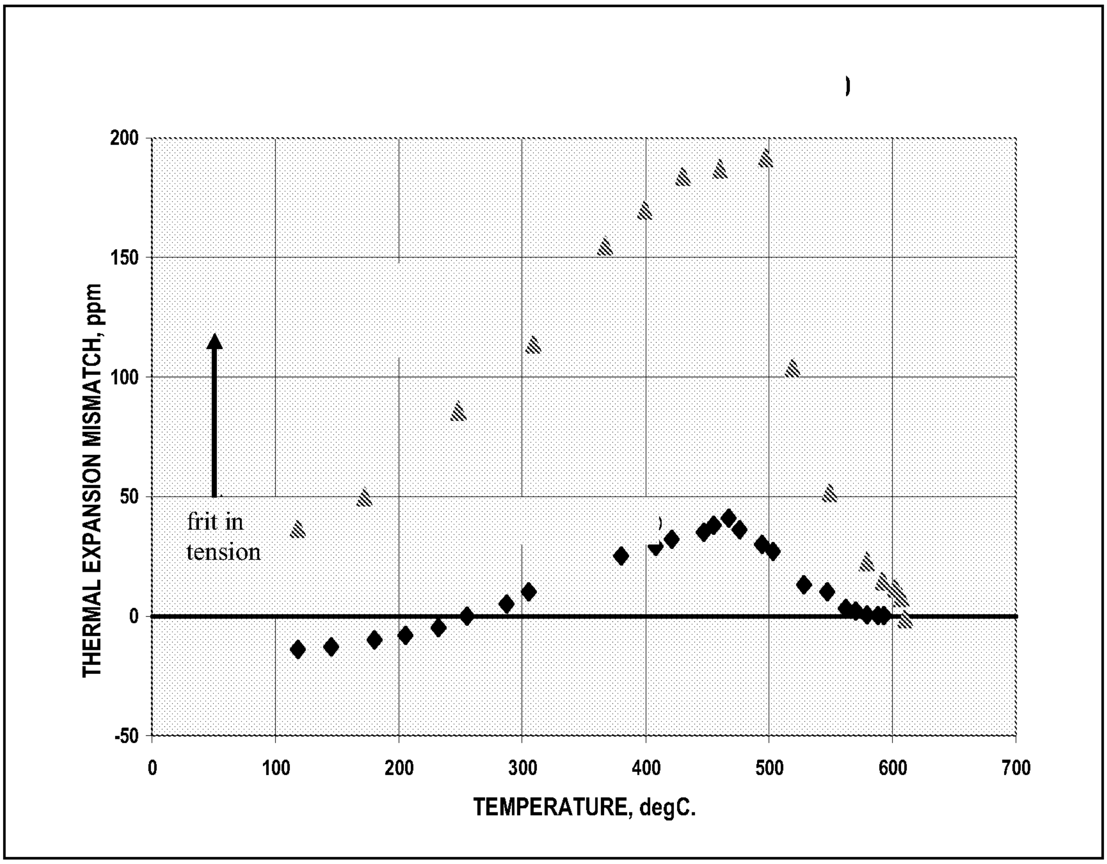

200
150
100
50
0
-50
THERMAL EXPANSION MISMATCH, ppm
frit in
tension
0
100
200
300
400
500
600
700
TEMPERATURE, degC.

Figure 12

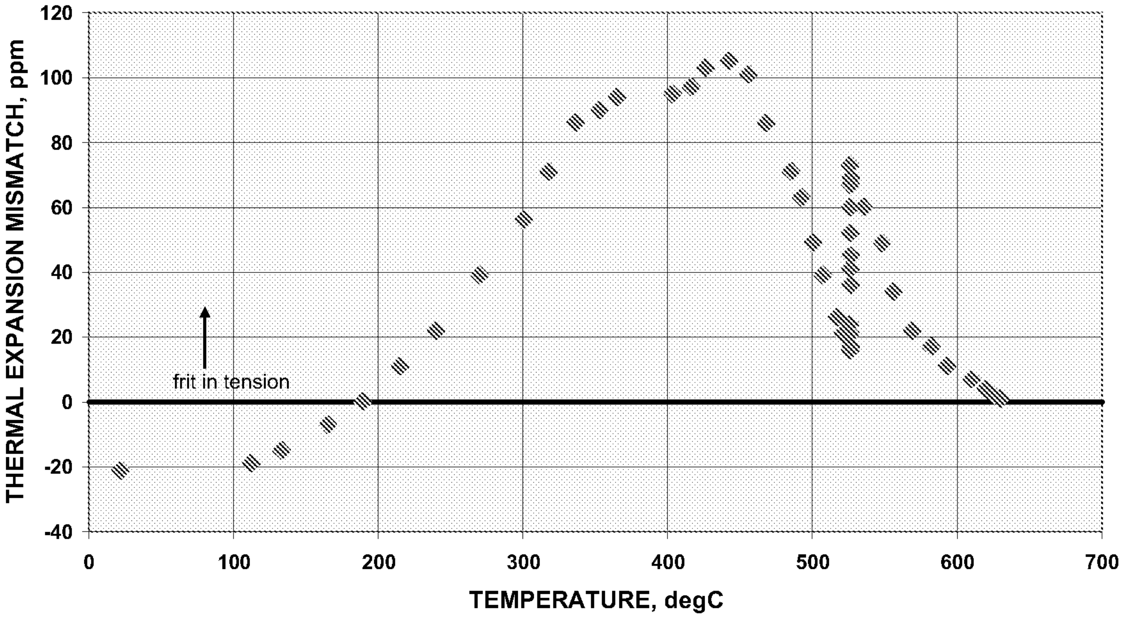

THERMAL EXPANSION MISMATCH, ppm
120
100
80
60
40
20
0
-20
-40
frit in tension
0
100
200
300
400
500
600
700
TEMPERATURE, degC

Figure 13

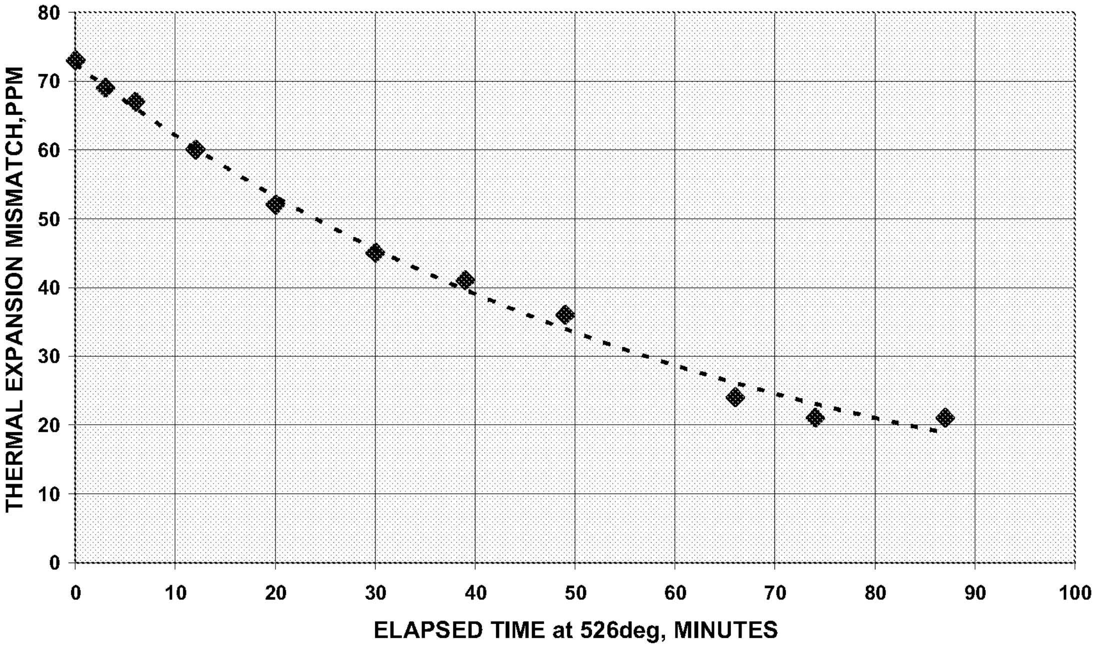
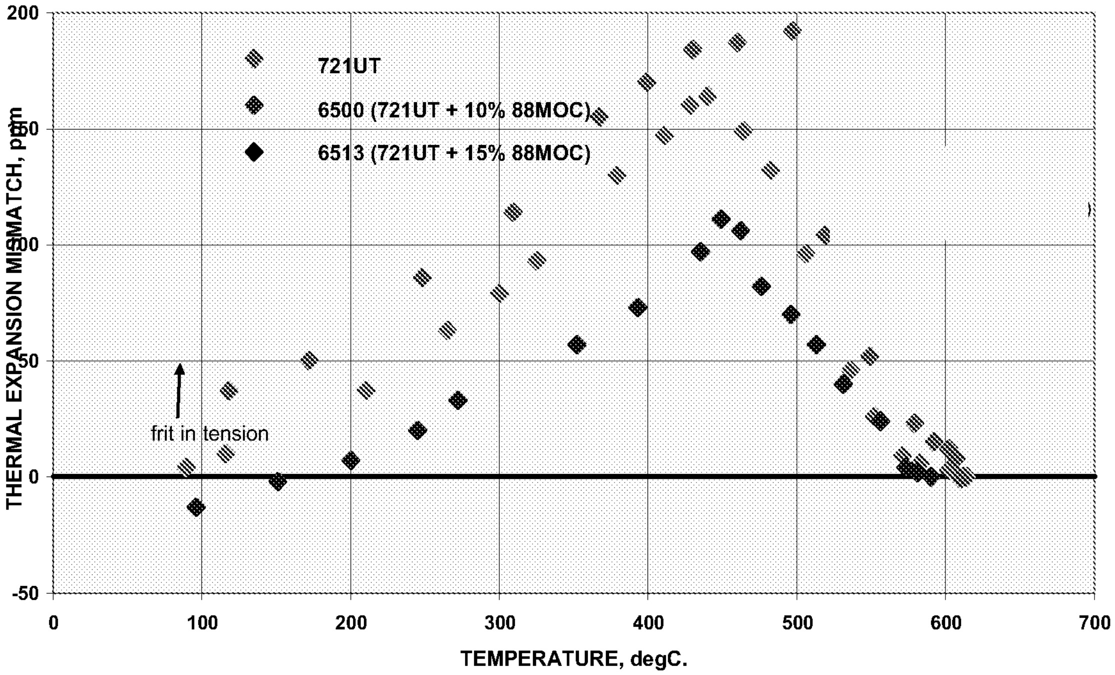

80
70
60
50
40
30
20
10
0
THERMAL EXPANSION MISMATCH,PPM
0
10
20
30
40
50
60
70
80
90
100
ELAPSED TIME at 526deg, MINUTES

Figure 14


200
150
100
50
0
-50
0
100
200
300
400
500
600
700
THERMAL EXPANSION MISMATCH, ppm
TEMPERATURE, degC.
721UT
6500 (721UT + 10% 88MOC)
6513 (721UT + 15% 88MOC)
frit in tension

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/069107

A. CLASSIFICATION OF SUBJECT MATTER
INV. C03C3/089 B01J19/00 B01L3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C03C B01J B01L

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 374 595 A (DUMBAUGH, JR. ET AL) 20 December 1994 (1994-12-20) column 4, line 19 - column 5, line 31; claims 1-26; tables I,II	1-18
Y	WO 99/40038 A (CORNING INCORPORATED) 12 August 1999 (1999-08-12) page 4, line 3 - page 5, line 27; claims 1-27	1-18
Y	US 6 461 734 B1 (CARRE ALAIN R. E) 8 October 2002 (2002-10-08) column 2, line 45 - column 4, line 19; claims 1-23; tables 1-3	1-18

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search 19 April 2007	Date of mailing of the international search report 02/05/2007
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Maurer, Renate

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/069107

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	EP 0 947 246 A (CORNING INCORPORATED) 6 October 1999 (1999-10-06) page 3, line 6 - page 4, line 57; claims 1-18	1-18
Y	DE 103 37 362 A1 (SCHOTT GLAS) 4 March 2004 (2004-03-04) page 2, paragraph 14 - page 3, paragraph 27 page 4, paragraph 36 - page 5, paragraph 52; claims 1-18	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/069107

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