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(54) Title: TRANSPARENT ARMOR COMPOSITES AND METHODS OF MAKING SAME

(57) Abstract: Transparent armor composites, and methods of making transparent armor composites comprising a first layer comprising a glass or glass-ceramic, a force dissipating material, and a bond that affixes at least a portion of the first layer to the second layer. The glass or glass-ceramic has an in-line transmission of at least 50 percent of theoretical maximum.

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TRANSPARENT ARMOR COMPOSITES AND METHODS OF MAKING SAME

Cross Reference To Related Application

This application claims the benefit of U.S. Provisional Patent Application No. 60/747,479, filed May 17, 2006, the disclosure of which is incorporated by reference herein in its entirety.

FIELD OF INVENTION

[0001] The present disclosure relates generally to transparent armor. More particularly, the present disclosure relates to transparent glass and glass-ceramic composites, and methods of making transparent glass and glass-ceramic composites.

BACKGROUND

[0002] Various transparent armor materials designed to resist the incursion of small arms projectiles and shrapnel are known. These transparent armor materials can be made from oxide glass systems and plastic layers bonded together to form laminated composites.

[0003] The majority of oxide glass systems utilize well-known glass-formers such as SiO₂, B₂O₃, P₂O₅, GeO₂, and TeO₂ to aid in the formation of the glass. WIPO Publication Number WO 2003/011776 and Rosenflanz *et al.*, Bulk glasses and ultrahard nanoceramics based on alumina and rare-earth oxides, *Nature* **430**, 761-64 (2004), report novel bulk glass and glass-ceramic compositions that can be formed by consolidating glass bodies (e.g., a plurality of glass beads) that exhibit T_g and T_x. There is a continuing desire to develop new uses and applications for these novel glass and glass-ceramic materials.

SUMMARY

[0004] The present disclosure relates generally to transparent armor. More particularly, the present disclosure relates to transparent glass and glass-ceramic composites, and methods of making transparent glass and glass-ceramic composites.

[0005] In one embodiment of the present disclosure is a transparent composite material having a first layer comprising a glass comprising a first metal oxide and a second metal oxide, wherein the first metal oxide and the second metal oxide are different from one another, the glass having a T_g and T_x , wherein the difference between T_g and T_x is at least 5 degrees Celsius, wherein the glass has an in-line transmission of at least 50 percent of theoretical maximum, wherein the glass has x, y, and z dimensions each perpendicular to each other, and each of the x and y dimensions is at least 25 mm, and wherein the glass contains not more than 20 percent by weight SiO_2 , not more than 20 percent by weight B_2O_3 , and not more than 40 percent by weight P_2O_5 , based on the total weight of the glass. The composite material has a second layer comprising a force dissipating material, and a bond material that affixes at least a portion of the first layer to the second layer.

[0006] In another embodiment of the present disclosure is a transparent composite material having a first layer comprising a glass-ceramic comprising a first metal oxide selected from the group consisting of Al_2O_3 , CaO , CoO , Cr_2O_3 , CuO , Fe_2O_3 , HfO_2 , MgO , MnO , Nb_2O_5 , NiO , REO , Sc_2O_3 , Ta_2O_5 , TiO_2 , V_2O_5 , Y_2O_3 , ZnO , ZrO_2 , and complex metal oxides thereof, and a second metal oxide selected from the group consisting of Al_2O_3 , Bi_2O_3 , CaO , CoO , Cr_2O_3 , CuO , Fe_2O_3 , Ga_2O_3 , HfO_2 , MgO , MnO , Nb_2O_5 , NiO , REO , Sc_2O_3 , Ta_2O_5 , TiO_2 , V_2O_5 , Y_2O_3 , ZnO , ZrO_2 , and complex metal oxides thereof, wherein the first metal oxide and the second metal oxide are different from one another, wherein the glass-ceramic comprises an in-line transmission of at least 50 percent of theoretical maximum, wherein the glass-ceramic has x, y, and z dimensions each perpendicular to each other, and each of the x and y dimensions is at least 25 mm, and wherein the glass contains not more than 20 percent by weight SiO_2 , not more than 20 percent by weight B_2O_3 , and not more than 40 percent by weight P_2O_5 , based on the total weight of the glass. The composite material has a second layer comprising a force dissipating material, and a bond material that affixes at least a portion of the first layer to the second layer.

[0007] Another embodiment of the present disclosure is a method for determining an end-point for a heat-treatment protocol to optimize hardness and in-line transmission of the resulting transparent armor composite. Surprisingly, it was found that glass-ceramic precursors of the present disclosure exhibited a transition point (i.e., a Transmission Loss Point, as defined herein) that facilitates optimization of hardness and in-line transmission of the glass-ceramic. The Transmission Loss Point can be determined by generating a

series of data and evaluated the data to determine the point at which any further progression in the heat-treatment protocol (e.g., increase in temperature and/or residence time) results in an irreversible and marked decline in in-line transmission.

[0008] Using the methods of the present disclosure, transparent armor composites can be made with a combination of high hardness and high in-line transmission (i.e., at least 50% of theoretical maximum). The transparent armor composites of the present disclosure can be used in a variety of applications, including, for example, as windows on military and armored vehicles (cars, jeeps, trucks, aircraft, tanks, trains, ships, amphibious vehicles, etc.), and in personal protection equipment such as goggles and face-shields. The transparent armor composites can also be used for stationary objects that require transparency, including building windows, doors, bus stops, shelters, etc.

[0009] In this application:

[0010] “amorphous material” refers to material derived from a melt and/or a vapor phase that lacks any long range crystal structure as determined by X-ray diffraction and/or has an exothermic peak corresponding to the crystallization of the amorphous material as determined by DTA (differential thermal analysis);

[0011] “ceramic” includes glass, crystalline ceramic, and combinations thereof;

[0012] “complex metal oxide” refers to a metal oxide comprising two or more different metal elements and oxygen (e.g., $\text{CeAl}_{11}\text{O}_{18}$, $\text{Dy}_3\text{Al}_5\text{O}_{12}$, MgAl_2O_4 , and $\text{Y}_3\text{Al}_5\text{O}_{12}$);

[0013] “differential thermal analysis” or “DTA” refers to a procedure that involves measuring the difference in temperature between a sample and a thermally inert reference, such as Al_2O_3 , as the temperature is raised. A graph of the temperature difference as a function of the temperature of the inert reference provides information on exothermic and endothermic reactions taking place in the sample. An exemplary instrument for performing this procedure is available from Netzsch Instruments, Selb, Germany under the trade designation “NETZSCH STA 409 DTA/TGA”. A suitable amount, e.g., 400 mg, of a sample can be placed in a suitable inert holder (e.g. a 100 ml Al_2O_3 sample holder) and heated in static air at a suitable rate, e.g. $10^\circ\text{C}/\text{minute}$, from an initial temperature (e.g. room temperature, or about 25°C) to a final temperature, such as 1200°C ;

[0014] “glass” refers to amorphous material exhibiting a glass transition temperature;

[0015] “glass-ceramic” refers to ceramic comprising crystals formed by heat-treating glass;

[0016] “glass-ceramic precursor” refers to the glass body that is subjected to heat-treatment to form a glass-ceramic;

[0017] “heat-treatment protocol” refers to all processing parameters (e.g., temperature, time, pressure, etc.) of the heat-treatment process;

[0018] “ T_g ” refers to the glass transition temperature as determined by DTA (differential thermal analysis);

[0019] “ T_x ” refers to the crystallization temperature as determined by DTA (differential thermal analysis);

[0020] “Transmission Loss Point” refers to the onset point for a given glass heat-treatment protocol at which further progression in the heat-treatment protocol (e.g., increase in temperature and/or residence time) causes an irreversible and marked decline in in-line transmission. The Transmission Loss Point for a composition is unique for a given heat-treatment protocol; and

[0021] “rare earth oxides” or “REO” refers to cerium oxide (e.g., CeO_2), dysprosium oxide (e.g., Dy_2O_3), erbium oxide (e.g., Er_2O_3), europium oxide (e.g., Eu_2O_3), gadolinium oxide (e.g., Gd_2O_3), holmium oxide (e.g., Ho_2O_3), lanthanum oxide (e.g., La_2O_3), lutetium oxide (e.g., Lu_2O_3), neodymium oxide (e.g., Nd_2O_3), praseodymium oxide (e.g., Pr_6O_{11}), samarium oxide (e.g., Sm_2O_3), terbium oxide (e.g., Tb_2O_3), thorium oxide (e.g., Th_4O_7), thulium oxide (e.g., Tm_2O_3), and ytterbium oxide (e.g., Yb_2O_3), and combinations thereof.

[0022] Further, it is understood herein that unless it is stated that a metal oxide (e.g., Al_2O_3 , complex Al_2O_3 -metal oxide, etc.) is crystalline, for example, in a glass-ceramic, it may be glass, crystalline, or portions glass and portions crystalline. For example, if a glass-ceramic comprises Al_2O_3 and ZrO_2 , the Al_2O_3 and ZrO_2 may each be in a glassy state, crystalline state, or portions in a glassy state and portions in a crystalline state, or even as a reaction product with another metal oxide(s) (e.g., unless it is stated that, for example, Al_2O_3 is present as crystalline Al_2O_3 or a specific crystalline phase of Al_2O_3 (e.g., alpha Al_2O_3), it may be present as crystalline Al_2O_3 and/or as part of one or more crystalline complex Al_2O_3 -metal oxides).

[0023] The above summary of making transparent armor composites according to the present disclosure is not intended to describe each disclosed embodiment of every

implementation of making transparent armor composites according to the present disclosure. The detailed description that follows more particularly exemplify illustrative embodiments. The recitation of numerical ranges by endpoints includes all numbers subsumed with that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 4, 4.80, and 5).

DETAILED DESCRIPTION

[0024] The transparent armor composite of the present disclosure comprises at least two layers bonded together by a bond material. The first layer comprises a glass or glass-ceramic material with a high hardness that serves as a first line of defense when the composite is subjected to elements of an adverse environment (e.g., shock, scratching, abrasion, adverse weather conditions, etc.). In addition, the first layer may deform a projectile, thereby reducing the resulting impact on the armor composite.

[0025] WIPO Publication Number WO 2003/011776 and Rosenflanz *et al.*, Bulk glasses and ultrahard nanoceramics based on alumina and rare-earth oxides, *Nature* **430**, 761-64 (2004), report novel glass compositions that can be used to form glass and glass-ceramic useful in making the first layer of the transparent armor composite according to the present disclosure, and are incorporated herein by reference. Glass and glass-ceramic precursors useful in making the first layer according to the present disclosure can also be obtained by other techniques, such as direct melt casting, melt atomization, containerless levitation, laser spin melting, and other methods known to those skilled in the art (see, e.g., Rapid Solidification of Ceramics, Brockway et al., Metals And Ceramics Information Center, A Department of Defense Information Analysis Center, Columbus, OH, January, 1984).

[0026] The glass or glass-ceramic of the first layer generally comprises a mixture of at least two metal oxides (or complex metal oxides). Metal oxides that may be used to form the glass or glass-ceramic include, for example, Al_2O_3 ; TiO_2 ; rare earth oxides (REO's) such as CeO_2 , Dy_2O_3 , Er_2O_3 , Eu_2O_3 , Gd_2O_3 , Ho_2O_3 , La_2O_3 , Lu_2O_3 , Nd_2O_3 , Pr_6O_{11} , Sm_2O_3 , Tb_2O_3 , Th_4O_7 , Tm_2O_3 and Yb_2O_3 ; ZrO_2 , HfO_2 , Ta_2O_5 , Nb_2O_5 , Bi_2O_3 , WO_3 , V_2O_5 , Ga_2O_3 , and alkaline earth metal oxides such as CaO and BaO . Examples of useful glass and glass-ceramics for making transparent armor composites according to the present disclosure include those comprising REO- TiO_2 , REO- ZrO_2 - TiO_2 , REO- Al_2O_3 , REO-

Al₂O₃-ZrO₂, and REO-Al₂O₃-ZrO₂-SiO₂ glasses. Useful glass formulations include those at or near a eutectic composition.

[0027] In addition to these compositions and compositions disclosed in WIPO Publication Numbers WO 2003/011781, WO 2003/011776, WO 2005/061401, U.S. Patent Application having Serial No. 11/273,513, filed November 14, 2005 (Attorney Docket No. 61351US002), and Rosenflanz *et al.*, Bulk glasses and ultrahard nanoceramics based on alumina and rare-earth oxides, *Nature* **430**, 761-64 (2004), which are incorporated herein by reference, other compositions, including eutectic compositions, will be apparent to those skilled in the art after reviewing the present disclosure.

[0028] In some embodiments, the first and second metal oxides are each selected from the group consisting of Al₂O₃, Bi₂O₃, CaO, CoO, Cr₂O₃, CuO, Fe₂O₃, Ga₂O₃, HfO₂, MgO, MnO, Nb₂O₅, NiO, REO, Sc₂O₃, Ta₂O₅, TiO₂, V₂O₅, Y₂O₃, ZnO, ZrO₂, and complex metal oxides thereof.

[0029] In some embodiments, a first metal oxide is selected from the group consisting of Al₂O₃, CaO, CoO, Cr₂O₃, CuO, Fe₂O₃, HfO₂, MgO, MnO, Nb₂O₅, NiO, REO, Sc₂O₃, Ta₂O₅, TiO₂, V₂O₅, Y₂O₃, ZnO, ZrO₂, and complex metal oxides thereof, and a second metal oxide is selected from the group consisting of Al₂O₃, Bi₂O₃, CaO, CoO, Cr₂O₃, CuO, Fe₂O₃, Ga₂O₃, HfO₂, MgO, MnO, Nb₂O₅, NiO, REO, Sc₂O₃, Ta₂O₅, TiO₂, V₂O₅, Y₂O₃, ZnO, ZrO₂, and complex metal oxides thereof. In some embodiments, the first metal oxide is selected from the group consisting of Al₂O₃, REO, TiO₂, Y₂O₃, ZrO₂, and complex metal oxides thereof.

[0030] In some instances, it may be preferred to incorporate limited amounts of oxides selected from the group consisting of: B₂O₃, GeO₂, P₂O₅, SiO₂, TeO₂, and combinations thereof. These metal oxides, when used, are typically added in the range of 0 to 20 (in some embodiments 0 to 15, 0 to 10, or even 0 to 5) percent of the glass or glass-ceramic depending, for example, upon the desired property.

[0031] In some embodiments, the glass or glass-ceramic comprises at least 20 (in some embodiments, preferably at least 25, 30, 35, 40, 45, 50, 55, 60, 65, 70 or even at least 75) percent by weight Al₂O₃, based on the total weight of the glass or glass-ceramic, and a metal oxide other than Al₂O₃ (e.g., Bi₂O₃, CaO, CoO, Cr₂O₃, CuO, Fe₂O₃, Ga₂O₃, HfO₂, MgO, MnO, Nb₂O₅, NiO, REO, Sc₂O₃, Ta₂O₅, TiO₂, V₂O₅, Y₂O₃, ZnO, ZrO₂, and complex metal oxides thereof).

[0032] In some embodiments, the glass or glass-ceramic precursor is formed by coalescing a plurality of glass bodies (e.g., beads) comprising a first metal oxide and a second metal oxide, wherein the difference between T_g and T_x is at least 5 degrees Celsius, and wherein the glass bodies contain not more than 20 (in some embodiments 15, 10, 5, 3, 2, or even 1) percent by weight SiO_2 , not more than 20 (in some embodiments 15, 10, 5, 3, 2, or even 1) percent by weight B_2O_3 , and not more than 40 (in some embodiments 30, 20, 10, 5, 3, 2, or even 1) percent by weight P_2O_5 , based on the total weight of the glass bodies. The coalescing step can be conducted by applying heat and/or pressure to the plurality of glass bodies. WIPO Publication Number WO 2003/011776, incorporated herein by reference, discloses methods for coalescing a plurality of glass bodies. The coalescing process can be used to shape the glass-ceramic precursor to a desired geometry. The glass-ceramic precursor can also be shaped using methods reported in copending application having U.S. Serial No. 60/797,847 (Attorney Docket No. 62097US002), entitled "Method of Reshaping a Glass Body", filed May 3, 2006, the disclosure of which is incorporated herein by reference.

[0033] In some embodiments, a combination of glass bodies that vary in composition and/or size can be coalesced to form the glass or glass-ceramic precursor. The chosen compositions may be varied to create a glass with discontinuous properties. The glass bodies that vary in composition may be uniformly mixed prior to coalescing or the glass bodies that vary in composition may be purposely segregated, for example, to form distinct layers or three-dimensional formations within the resulting article. For instance, depending upon the composition of the glass bodies and/or process conditions, after coalescing the resulting article may comprise distinct layers. These layers can be alternated to achieve a desired result. Conversely, after coalescing there may be migration of one layer into the other layer. The composition of the glass bodies and/or processing can be optimized to change any migration effect.

[0034] In one example, the glass body compositions can be chosen and oriented such that the outer portion (i.e., the surface opposite the bond material) of the glass or glass-ceramic may contain a harder composition and the inner portion (i.e., surface proximate the bond material and second layer) may have higher strength.

[0035] The glass bodies to be coalesced can also be mixed with non-glass materials to create a composite glass or glass-ceramic. Examples of such non-glass materials include:

metals (e.g., aluminum, carbon steel, etc.) crystalline metal oxides (alumina, silica, zirconia, rare earth oxides, yttria, magnesia, calcia, etc.), metal carbides, metal nitrides, metal borides, diamond and the like. The non-glass material should not degrade upon the temperatures and pressures of coalescing and heat-treatment. The composition of the composite glass-ceramic precursors may adversely affect the in-line transmission and/or hardness of the resulting glass-ceramic.

[0036] In general, glasses that can be used to form glass or glass-ceramic for making transparent armor composites according to the present disclosure can be made by heating the appropriate metal oxide sources to form a melt, desirably a homogenous melt, and then cooling the melt to provide glass. Some embodiments of glass materials can be made, for example, by melting the metal oxide sources in any suitable furnace (e.g., an inductive heated furnace, a gas-fired furnace, or an electrical furnace), or, for example, in a flame or plasma. The resulting melt is cooled by discharging the melt into any of a number of types of cooling media such as high velocity air jets, liquids, graphite or metal plates (including chilled plates), metal rolls (including chilled metal rolls), metal balls (including chilled metal balls), and the like.

[0037] In one method, glasses that can be used to form the first layer of transparent armor composites according to the present disclosure can be made utilizing flame fusion as disclosed, for example, in U.S. Pat. No. 6,254,981, incorporated by reference. Briefly, the metal oxide source materials are formed into particles sometimes referred to as “feed particles”. Feed particles are typically formed by grinding, agglomerating (e.g., spray-drying), melting, or sintering the metal oxide sources. The size of the feed particles fed into the flame generally determines the size of the resulting amorphous particle material. The feed particles are fed directly into a burner such as a methane-air burner, an acetylene-oxygen burner, a hydrogen-oxygen burner, and like. The materials are subsequently quenched in, for example, water, cooling oil, air, or the like.

[0038] Other techniques for forming melts, cooling/quenching melts, and/or otherwise forming glass include vapor phase quenching, plasma spraying, melt-extraction, gas or centrifugal atomization, thermal (including flame or laser or plasma-assisted) pyrolysis of suitable precursors, physical vapor synthesis (PVS) of metal precursors, and mechanochemical processing.

[0039] The cooling rate is believed to affect the properties of the quenched amorphous material. For instance, glass transition temperature, density and other properties of glass typically change with cooling rates. Rapid cooling may also be conducted under controlled atmospheres, such as a reducing, neutral, or oxidizing environment to maintain and/or influence the desired oxidation states, etc., during cooling. The atmosphere can also influence glass formation by influencing crystallization kinetics from undercooled liquid.

[0040] In embodiments using a glass-ceramic as the first layer, heat-treatment of the glass-ceramic precursor can be carried out in any of a variety of ways, including those known in the art for heat-treating glass to provide glass-ceramics. For example, heat-treatment can be conducted in batches, for example, using resistive, inductively or gas heated furnaces. The temperature may range anywhere from 800°C to 1600°C, typically between 900°C to 1400°C. It is also within the scope of the present invention to perform some of the heat-treatment in batches (e.g., for the nucleation step) and another continuously (e.g., for the crystal growth step and to achieve the desired density). For the nucleation step, the temperature typically ranges between about 900°C to about 1100°C, in some embodiments, preferably in a range from about 925°C to about 1050°C. This heat treatment may occur, for example, by feeding the material directly into a furnace at the elevated temperature. Alternatively, for example, the material may be fed into a furnace at a much lower temperature (e.g., room temperature) and then heated to desired temperature at a predetermined heating rate. The heat-treatment can be conducted in an atmosphere other than air. In some cases it might be even desirable to heat-treat in a reducing atmosphere(s). Also, for, example, it may be desirable to heat-treat under gas pressure as in, for example, hot-isostatic press, or in gas pressure furnace.

[0041] In some embodiments, the target heat-treatment protocol for making a glass-ceramic article is determined by subjecting a plurality of test glass bodies to various extents of an experimental heat-treatment protocol. The term “target heat-treatment protocol” refers to the actual heat-treatment protocol that is used to heat-treat a glass-ceramic precursor to form a desired glass-ceramic article. The term “experimental heat-treatment protocol” refers to a heat-treatment protocol that is used to develop the target heat-treatment protocol by subjecting a plurality of test glass bodies to various extents of the experimental heat-treatment protocol in order to identify the Transmission Loss Point. The target heat-treatment protocol corresponds with the experimental heat-treatment

protocol up to the end point of the target heat-treatment protocol, at which point the experimental heat-treatment protocol typically continues to progress (i.e., subjects the sample to further heat-treatment).

[0042] The heat-treatment protocol used to heat-treat glass-ceramic precursors in accordance with the present disclosure can be any protocol developed by those skilled in the art. For example, the heat-treatment protocol may include a temperature that increases at a constant rate (per unit time) while other variables are held constant. In other embodiments, the heat-treatment protocol may include a constant temperature and the extent of the heat-treatment is determined principally by the samples residence time. In yet further embodiments, the heat-treatment protocol includes temperature changes in steps. In yet further embodiments, the heat-treatment protocol has a constant residence time, a constant starting temperature, and the rate of temperature increases varies. In even further embodiments, multiple variables in the heat-treatment process change during the progression of the heat-treatment protocol.

[0043] In certain embodiments, the heat-treatment protocol may comprise at least two stages. The first stage comprising heating to a temperature near the first crystallization temperature (± 50 degrees) of the glass and holding the temperature for at least 1 minute, 5 minutes, 20 minutes or even 1 hour to at least crystallize a portion of the glass. The second stage comprises heating at essentially any rate and encompassing temperatures higher than the first stage holding temperature. In some embodiments, the glass-ceramic can be cooled from the holding temperature of the first stage to about room temperature and then reheated in a second stage. In some embodiments, conducting heat-treatment in accordance with a two stage protocol has been found to reduce cracking and warpage of the article. In certain embodiments this target protocol is also beneficial for minimizing total heat-treatment time, thus improving manufacturability.

[0044] After submitting the test glass bodies to various extents of the target heat-treatment protocol, the heat-treated test bodies can be evaluated for in-line transmission and optionally, hardness. The in-line (and optionally, hardness) data is then evaluated to determine the target heat-treatment-protocol to be applied to the glass-ceramic precursor to make the first layer of the transparent armor composite.

[0045] As hardness generally increases as the heat-treatment protocol proceeds, it may not be necessary to measure hardness to evaluate the resulting data to determine a target heat-treatment protocol.

[0046] In-line transmission of a sample can be determined using a conventional spectrophotometer such as Perkin Elmer Lambda 900 Spectrophotometer. Generally, transmission of optically homogeneous materials in the absence of absorption and scattering is limited only by the material-specific reflection $R = ((n-1)/(n+1))^2$ at the front and back side and is dependent on refractive index, n only. The theoretical maximum value of transmission T_{th} is $(1-R)^2$. In the context of the present disclosure and appended claims, the in-line transmission value of a material is determined by measuring a 1.2 millimeter thick sample at a light wavelength between 600 and 650 nm.

[0047] The test glass bodies preferably have the same chemical and physical properties as the glass-ceramic precursor used to form the first layer of the transparent armor composite. In other embodiments, the chemical and physical properties of the test glass bodies are substantially the same as the chemical and physical properties of the glass-ceramic precursor used to form the transparent armor composite. In yet further embodiments, the dimensions of the test glass bodies vary from the dimensions of the glass-ceramic precursor used to form the transparent armor composite. Variations between the physical and/or chemical properties of the test glass bodies and the glass-ceramic precursor used to form the transparent armor composite can be accounted for using information gathered from comparative experiments, as well as information and technical assessments known by those skilled in the art.

[0048] The in-line transmission (and optionally, hardness) data can be evaluated in a variety of ways depending on the desired properties of the glass-ceramic article. In some embodiments, a minimum in-line transmission value of the glass-ceramic article is required and it is desired to obtain a maximum hardness. In this scenario, the data can be evaluated by determining the heat-treatment protocol that provides maximum hardness while maintaining the minimum in-line transmission.

[0049] In other embodiments, it is desired to substantially optimize the in-line transmission and hardness of the glass-ceramic. In the context of the present disclosure, the in-line transmission and hardness are considered substantially optimized when any

further progression in the heat-treatment protocol (e.g., increase in temperature and/or residence time) results in an irreversible and marked decline in in-line transmission.

[0050] In some embodiments, the in-line transmission (and optionally, hardness) data of the test bodies is evaluated to determine the Transmission Loss Point of the heat-treatment protocol. The heat-treatment protocol can then be followed until its Transmission Loss Point to make the transparent armor composite. In some embodiments it may be desirable to exceed the Transmission Loss Point to form yet harder materials with lower in-line transmission. In this case, the target heat-treatment protocol proceeds beyond the Transmission Loss Point to achieve a desired combination of hardness and in-line transmission.

[0051] In some embodiments, the first layer of the transparent armor composite is a glass-ceramic that has an in-line transmission within 30 (in some embodiments 25, 20, 15, 10, or even 5) percent of the in-line transmission of the glass-ceramic at the Transmission Loss Point. In other embodiments, the first layer of the transparent armor composite is subject to a heat-treatment protocol that includes heating at a temperature that is within 50 (in some embodiments 40, 30, 20, or even 10) degrees Celsius of the temperature of the Transmission Loss Point of the target heat-treatment protocol.

[0052] In some embodiments, the glass or glass-ceramic first layer of the transparent armor composite made according to methods of the present disclosure has an in-line transmission that is at least 50 (in some embodiments 55, 60, 65, or even 70) percent of theoretical maximum. In some embodiments, the glass or glass-ceramic first layer of the transparent armor composite made according to methods of the present disclosure has a hardness of at least 11 (in some embodiments preferably, at least 14, 15, 16, 17, or even at least 18) GPa. In some embodiments, the glass-ceramic of the first layer made according to methods of the present disclosure has Young's modulus of at least 140 (in some embodiments at least 150, 175, 200, or even 250) GPa.

[0053] The first layer of the transparent armor composite made according to methods of the present disclosure can be made in a variety of sizes and shapes, depending on the desired application. In some embodiments, the first layer of the transparent armor composite has x, y, and z dimensions, each perpendicular to each other, and each of the x and y dimensions is at least 25 (in some embodiments 50, 100, 500, or even 1000 or

greater) millimeters. In some embodiments, the z dimension is at least 0.5 (in some embodiments 1, 2, 3, 5, 10, 25, or even 100) millimeters.

[0054] The second layer of the transparent armor composite comprises a force dissipating material. The force dissipating material can be any material known to those skilled in the art, including, for example, polycarbonate, polyacrylic (including cast acrylic, polymethylmethacrylate, modified acrylics and the like), cellulose acetate butyrate, ionomers, nylons, polyolefins, polyesters, polyurethane (thermosetting and thermoplastic), combinations thereof and the like. In some preferred embodiments, the force dissipating material comprises polycarbonate or a polyacrylic.

[0055] In some embodiments, the force dissipating material may also contain a protective hard coating on the surface opposite the bond material. The force dissipating layer typically ranges in thickness from 0.1 to 100 (in some embodiments, 0.5 to 50) millimeters thick. The force dissipating material may comprise a plurality of layers of the same or different materials bonded together to form a thicker layer.

[0056] The bond material used to affix the first layer to the second layer can be any bond material known to those skilled in the art, including, for example, polyurethane adhesives, polybutyl vinyl, thermosetting resins, UV curable resins, acrylic adhesives, combinations thereof, and the like.

[0057] The bond material can be applied uniformly across a substantial portion of the interface between the first and second layers, or can be applied to select portions of the interface. The bond material can be applied using application and/or laminating methods known to those skilled in the art.

[0058] In another embodiment of the present disclosure, the transparent armor composite may further include additional layers, including, for example, a layer of silica based glass such as OEM safety glass, OEM tempered glass, float glass or any other suitable silica based glass.

[0059] EXAMPLES

[0060] Example 1

[0061] A porcelain jar was charged with 1000 g of DI water, pH of which was adjusted to 4 using HNO_3 . Then the following oxide powders were added: 385g Al_2O_3 , 330g La_2O_3 , 100g Gd_2O_3 , and 185g ZrO_2 . The La_2O_3 powder was calcined at 700C for 6 hrs prior to batch mixing. About 2000 g of alumina milling media was added to the jar and the contents were milled for 72 hrs at 120 rpm. After milling, the resulting slurry was transferred into a glass beaker and stirred with a magnetic stirrer. Immediately after transferring the slurry into the beaker, 40 ml of 0.5M solution of NH_4Cl was added which led to thickening of the slurry into a gel-like consistency. This gelatine-like substance was then transferred into glass trays and dried in forced convection air oven at 250F. The obtained dried powder cake was further calcined at 1250C for 2h to completely remove any residual moisture.

[0062] After grinding with a mortar and pestle, the resulting screened particles were fed slowly (about 0.5 gram/minute) through a funnel, under a argon gas atmosphere 5 standard liter per minute (SLPM), into a hydrogen/oxygen torch flame which melted the particles and carried them directly into a 19-liter (5-gallon) rectangular container (41 centimeters (cm) by 53 cm by 18 cm height) of continuously circulating, turbulent water (20oC) to rapidly quench the molten droplets. The torch was a Bethlehem bench burner PM2D Model B obtained from Bethlehem Apparatus Co., Hellertown, PA. The torch had a central feed port (0.475 cm (3/16 inch) inner diameter) through which the feed particles were introduced into the flame. Hydrogen and oxygen flow rates for the torch were as follows. The hydrogen flow rate was 42 standard liters per minute (SLPM) and the oxygen flow rate was 18 SLPM. The angle at which the flame hit the water was approximately 90, and the flame length, burner to water surface, was approximately 38 centimeters (cm).

[0063] The resulting molten and quenched particles were collected in a pan and dried at 110C. The particles were spherical in shape and ranged in size from a few tens of micron to up to 250 μm . From the fraction of beads measuring between 125 microns to 63 microns, greater than 95% were clear when viewed by an optical microscope.

[0064] 5g of beads sized between 90 microns and 125 microns was placed in a graphite die (10 mm in diameter) and hot-pressed at 915C into a glass cylinder using 30 MPa of applied pressure. The glass cylinder was then sectioned into 1.2 mm thick disks that were polished to an optically smooth surface.

[0065] In-line transmission data were generated using a conventional spectrophotometer such as Perkin Elmer Lambda 900 Spectrophotometer, and was found to be about 55% for light of a wavelength between 600 and 650 nm. For the refractive index of the material of this example ($n=1.84$), the T_{th} is 83.9%. Therefore, in-line transmission of the glass material of this example was about 66% of the theoretical maximum value.

[0066] The hardness measurements were made using a conventional microhardness tester (obtained under the trade designation "MITUTOYO MVK-VL" from Mitutoyo Corporation, Tokyo, Japan) fitted with a Vickers indenter using a 500-gram indent load. The microhardness measurements were made according to the guidelines stated in ASTM Test Method E384 Test Methods for Microhardness of Materials (1991), the disclosure of which is incorporated herein by reference. The hardness values were averaged over 20 measurements. The average hardness was found to be 9.23 GPa +/- 0.12 GPa.

[0067] Glass disks prepared in the current example were further subjected to heat-treatment at various temperatures between 950°C and 1250°C in order to induce crystallization and increase hardness. Heat-treatment was conducted using a dilatometer available from Netzsch Instruments, Selb, Germany under the trade designation "NETZSCH STA 409 DTA/TGA". Sample is placed in an Al_2O_3 sample holder and heated in static air at 10°C/minute, from an initial temperature (e.g. room temperature, or about 25°C) to a final temperature, such as 950°C.

[0068] Optical transmission and hardness were measured at each annealing temperature. The results are shown in Table 1.

[0069] Table 1

	Annealing Temperature, degrees C					
	950	1050	1075	1100	1150	1250
In-line Transmission, % theoretical	51.3	64.5	63.4	57.3	39.9	31
Hardness, GPa	10.2	12.5	12.8	13.0	14.0	15.8

[0070] Based on the results in Table 1, the temperature at the Transmission Loss Point for the chosen heat-treatment protocol is estimated to be around 1125 °C (the Transmission Loss Point could be determined more precisely by including additional annealing temperatures).

[0071] Example 2

[0072] About 200 g of beads was prepared as described in Example 1. 150 g of beads with fraction between 125 and 63 micrometers was placed into a 3 x 3" square die and hot-pressed at 925C under 20 MPa of applied load. The resultant material was a glass plate with thickness of about 6 mm. Hardness was determined to be 9.1 GPa +/-0.13 GPa.

[0073] The glass plate was secured in an aluminum frame holder with silicone rubber seal between the glass plate and the aluminum frame. The exposed area of the piece was 6.35 cm x 6.35 cm (2.5 x 2.5 inches). The thickness of the piece was 6 mm. This sample was tested using a 9 mm gas gun (rated to 1200 psi, manufacturer Physics Applications Inc. Dayton, Ohio). The projectile was a full metal jacket 9 mm round. The distance between the glass plate and the gun barrel's exit was 2.13 m (7 feet). The speed was measured with a "Model 35" Oehler chronograph (Oehler Research, Inc., Austin Texas). The speed measured was 850 feet per second. The glass plate broke upon impact but the projectile was stripped of its jacket, flattened and fragmented. The projectile was slowed down enough to be caught inside of a cardboard box behind the target holder.

[0074] It is to be understood that even in the numerous characteristics and advantages of making transparent armor composites set forth in above description and examples, together with details of the structure and function of the invention, the disclosure is illustrative only. Changes can be made to detail, especially in matters of glass composition within the principles of the invention to the full extent indicated by the meaning of the terms in which the appended claims are expressed and the equivalents of those structures and methods.

WHAT IS CLAIMED IS:

1. A composite transparent material comprising:
 - a first layer comprising a glass comprising a first metal oxide and a second metal oxide, wherein the first metal oxide and the second metal oxide are different from one another, the glass having a T_g and T_x , wherein the difference between T_g and T_x is at least 5 degrees Celsius, wherein the glass has an in-line transmission of at least 50 percent of theoretical maximum, wherein the glass has x, y, and z dimensions each perpendicular to each other, and each of the x and y dimensions is at least 25 mm, and wherein the glass contains not more than 20 percent by weight SiO_2 , not more than 20 percent by weight B_2O_3 , and not more than 40 percent by weight P_2O_5 , based on the total weight of the glass;
 - a second layer comprising a force dissipating material; and
 - a bond material that affixes at least a portion of the first layer to the second layer.
2. The composite transparent material of claim 1 wherein the first metal oxide and second metal oxide are selected from the group consisting of Al_2O_3 , Bi_2O_3 , CaO , CoO , Cr_2O_3 , CuO , Fe_2O_3 , Ga_2O_3 , HfO_2 , MgO , MnO , Nb_2O_5 , NiO , REO , Sc_2O_3 , Ta_2O_5 , TiO_2 , V_2O_5 , Y_2O_3 , ZnO , ZrO_2 , and complex metal oxides thereof.
3. The composite transparent material of claim 2 wherein the first metal oxide is selected from the group consisting of Al_2O_3 , REO , TiO_2 , Y_2O_3 , ZrO_2 , and complex metal oxides thereof.
4. The composite transparent material of claim 1 wherein the glass comprises not more than 20 percent by weight collectively B_2O_3 , GeO_2 , P_2O_5 , SiO_2 , TeO_2 , and combinations thereof, based on the total weight of the glass.
5. The composite transparent material of claim 1 wherein the force dissipating material comprises a material selected from the group consisting of polycarbonates, polyacrylics, cellulose acetate butyrate, nylon, polyolefins, polyesters, polyurethanes, and combinations thereof.

6. The composite transparent material of claim 1 wherein the bond material comprises a material selected from the group consisting of polyurethane adhesives, polybutyl vinyl, thermosetting resins, UV curable resins, acrylic adhesives, and combinations thereof.
7. A composite transparent material comprising:
 - a first layer comprising a glass-ceramic comprising a first metal oxide selected from the group consisting of Al_2O_3 , CaO , CoO , Cr_2O_3 , CuO , Fe_2O_3 , HfO_2 , MgO , MnO , Nb_2O_5 , NiO , REO , Sc_2O_3 , Ta_2O_5 , TiO_2 , V_2O_5 , Y_2O_3 , ZnO , ZrO_2 , and complex metal oxides thereof, and a second metal oxide selected from the group consisting of Al_2O_3 , Bi_2O_3 , CaO , CoO , Cr_2O_3 , CuO , Fe_2O_3 , Ga_2O_3 , HfO_2 , MgO , MnO , Nb_2O_5 , NiO , REO , Sc_2O_3 , Ta_2O_5 , TiO_2 , V_2O_5 , Y_2O_3 , ZnO , ZrO_2 , and complex metal oxides thereof, wherein the first metal oxide and the second metal oxide are different from one another, wherein the glass-ceramic comprises an in-line transmission of at least 50 percent of theoretical maximum, wherein the glass-ceramic has x, y, and z dimensions each perpendicular to each other, and each of the x and y dimensions is at least 25 mm, and wherein the glass contains not more than 20 percent by weight SiO_2 , not more than 20 percent by weight B_2O_3 , and not more than 40 percent by weight P_2O_5 , based on the total weight of the glass;
 - a second layer comprising a force dissipating material; and
 - a bond material that affixes at least a portion of the first layer to the second layer.
8. The composite transparent material of claim 7 wherein the first metal oxide is selected from the group consisting of Al_2O_3 , REO , TiO_2 , Y_2O_3 , ZrO_2 , and complex metal oxides thereof.
9. The composite transparent material of claim 7 wherein the glass-ceramic comprises not more than 20 percent by weight collectively B_2O_3 , GeO_2 , P_2O_5 , SiO_2 , TeO_2 , and combinations thereof, based on the total weight of the glass-ceramic.

10. The composite transparent material of claim 7 wherein the force dissipating material comprises a material selected from the group consisting of polycarbonates, polyacrylics, cellulose acetate butyrate, nylon, polyolefins, polyesters, polyurethanes, and combinations thereof.

11. The composite transparent material of claim 7 wherein the bond material comprises a material selected from the group consisting of polyurethane adhesives, polybutyl vinyl, thermosetting resins, UV curable resins, acrylic adhesives, and combinations thereof.

12. The composite transparent material of claim 7 wherein the glass-ceramic has a hardness of at least 11 GPa.

13. A method of making a composite transparent material comprising:
providing a glass-ceramic comprising a first metal oxide selected from the group consisting of Al_2O_3 , CaO , CoO , Cr_2O_3 , CuO , Fe_2O_3 , HfO_2 , MgO , MnO , Nb_2O_5 , NiO , REO , Sc_2O_3 , Ta_2O_5 , TiO_2 , V_2O_5 , Y_2O_3 , ZnO , ZrO_2 , and complex metal oxides thereof, and a second metal oxide selected from the group consisting of Al_2O_3 , Bi_2O_3 , CaO , CoO , Cr_2O_3 , CuO , Fe_2O_3 , Ga_2O_3 , HfO_2 , MgO , MnO , Nb_2O_5 , NiO , REO , Sc_2O_3 , Ta_2O_5 , TiO_2 , V_2O_5 , Y_2O_3 , ZnO , ZrO_2 , and complex metal oxides thereof, wherein the first metal oxide and the second metal oxide are different from one another, wherein the glass-ceramic comprises an in-line transmission of at least 50 percent of theoretical maximum, wherein the glass-ceramic has x, y, and z dimensions each perpendicular to each other, and each of the x and y dimensions is at least 25 mm, and wherein the glass contains not more than 20 percent by weight SiO_2 , not more than 20 percent by weight B_2O_3 , and not more than 40 percent by weight P_2O_5 , based on the total weight of the glass;
providing a force dissipating material;
applying a bond material to at least one of the glass-ceramic and the force dissipating material; and
laminating the glass-ceramic and the force dissipating material.

14. The method of claim 13 further comprising providing a plurality of glass bodies comprising a first metal oxide and a second metal oxide, wherein the first metal oxide and the second metal oxide are different from one another, the glass bodies having a T_g and T_x , wherein the difference between T_g and T_x is at least 5 degrees Celsius, and wherein the glass bodies contain not more than 20 percent by weight SiO_2 , not more than 20 percent by weight B_2O_3 , and not more than 40 percent by weight P_2O_5 , based on the total weight of the glass bodies;

heating the glass bodies above the T_g and coalescing at least a portion of the plurality of glass bodies to provide a bulk glass body; and

heat-treating the bulk glass body to form the glass-ceramic.

15. The method of claim 13 wherein the first metal oxide and second metal oxide are selected from the group consisting of Al_2O_3 , Bi_2O_3 , CaO , CoO , Cr_2O_3 , CuO , Fe_2O_3 , Ga_2O_3 , HfO_2 , MgO , MnO , Nb_2O_5 , NiO , REO , Sc_2O_3 , Ta_2O_5 , TiO_2 , V_2O_5 , Y_2O_3 , ZnO , ZrO_2 , and complex metal oxides thereof.

16. The method of claim 13 wherein the glass-ceramic comprises not more than 20 percent by weight collectively B_2O_3 , GeO_2 , P_2O_5 , SiO_2 , TeO_2 , and combinations thereof, based on the total weight of the glass-ceramic.

17. The method of claim 13 wherein the heat treating the bulk glass body comprises a target heat-treatment protocol selected to substantially optimize the in-line transmission and hardness of the glass-ceramic.

18. The method of claim 17 further comprising selecting an experimental heat-treatment protocol, subjecting a plurality of test bulk glass bodies to various extents of the experimental heat-treatment protocol, measuring in-line transmission of the heat-treated test bulk glass bodies to generate in-line transmission data, and using the in-line transmission data to select the target heat-treatment protocol.

19. The method of claim 13 wherein the bond material comprises a material selected from the group consisting of polyurethane adhesives, polybutyl vinyl, thermosetting resins, UV curable resins, acrylic adhesives, and combinations thereof.

20. The method of claim 13 wherein the force dissipating material comprises a material selected from the group consisting of polycarbonates, polyacrylics, cellulose acetate butyrate, nylon, polyolefins, polyesters, polyurethanes, and combinations thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2007/068550**A. CLASSIFICATION OF SUBJECT MATTER***C03C 17/28(2006.01)i, C03C 3/062(2006.01)i, C03C 3/064(2006.01)i, C03C 3/066(2006.01)i*

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)

IPC 8 : C03C 3/00~3/32, 6/00~6/10, 10/00~10/16, 27/00~27/12, B32B 17/00~17/12, 18/00

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

Korean Utility models and Applications for Utility model since 1975 : IPC 8 as above

Japaneses Utility models and Applications for Utility models since 1975 : IPC 8 as above

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

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 03/011786 A (3M INNOVATIVE PROPERTIES COMPANY) 13 FEBRUARY 2003 See abstract; page 4, line 15 - line 23; page 5, line 24 - page 11, line 31; page 24, line 7 - page 26, line 2; Table 1, 3, 5, 6	1-20
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Further documents are listed in the continuation of Box C.



See patent family annex.

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