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(54) Title: GLASSES AND CERAMICS WITH SELF-DISPERSED CORE-SHELL NANOSTRUCTURES VIA CASTING

(57) Abstract: Nanocomposite ceramic or glass materials are disclosed herein, which include a matrix material and one or more nanostructures dispersed within the matrix material. The nanostructures may comprise one or more core-shell nanostructures including a core nanostructure and a shell material. The shell material may be different from the material making up the core nanostructure and may improve the wettability of the core-shell nanostructure, the dispersion of the core-shell nanostructure within the matrix material, or make the core-shell nanostructure more resistant to oxidation, when compared to the core nanostructure alone. Methods of making nanocomposite ceramic or glass materials are also disclosed herein.



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GLASSES AND CERAMICS WITH SELF-DISPERSED CORE-SHELL NANOSTRUCTURES VIA CASTING

CORSS-REFERENCE TO RELATED PATENT APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 63/226,613, filed July 28, 2021, the contents of which is hereby incorporated by reference in its entirety.

BACKGROUND

[0002] Glasses and ceramics are important materials in nature and have significant societal value for their applications in daily life and industry, such as fine china, dental implants, electronics, chemicals, and manufacturing. This is due to their advantageous and desirable properties, including low density, high hardness, and chemical stability. However, ceramics are brittle because of their covalent and/or ionic bonds, and they often fail under about 1% to about 2% elastic strain. This has created a long-standing challenge for their processing and application as reliable product materials.

[0003] Ceramic matrix nanocomposites have been developed which include a high volume fraction of uniformly dispersed nanostructures. In these materials, nanostructures can be self-dispersed in ceramic melts, and bulk ceramics containing high loadings of the nanostructures can be cast from these ceramic melts. Although these materials relied on incorporation of semiconductor, carbide, or nitride nanoparticles into glasses as a proof-of-concept, scaling up their production up to commercially viable amounts is challenging for several reasons, including: poor wettability of the semiconductor, carbide, nitride, or boride particles in the glass matrix; relatively poor dispersion; and difficulty in avoiding oxidation at the high processing temperatures required to disperse the nanoparticles in the matrix. Thus, methods for improving the wettability, dispersion, and oxidation resistance of the nanostructures are of great commercial interest.

[0004] It is against this background that a need arose to develop the embodiments described herein.

SUMMARY

[0005] In one aspect, which may be combined with any other aspect or embodiment, the present disclosure relates to a nanocomposite ceramic or glass material, comprising: one or more matrix materials; and one or more nanostructures dispersed with the matrix material; wherein: the one or more nanostructures comprises a core-shell nanostructure.

[0006] In some embodiments, the core-shell nanostructure comprises a core material and a shell material coating the core nanostructure; and the shell material improves the wettability of the nanostructure by the matrix material and dispersion of the nanostructure within the matrix, relative to the core nanostructure alone.

[0007] In some embodiments, the shell material comprises the same material as the matrix material. In some embodiments, the core nanostructure comprises a carbon-based material.

[0008] In some embodiments, the nanostructure is present in the matrix material at a concentration (v/v) of at least about 1.0%. In some embodiments, the nanostructure is present in the matrix material at a concentration (v/v) of at least about 10%. In some embodiments, the nanostructure is present in the matrix material at a concentration (v/v) of at least about 20%.

[0009] In some embodiments, the nanocomposite ceramic or glass material has a fracture toughness of $2 \text{ MPa} \cdot \text{m}^{1/2}$ or greater. In some embodiments, the nanocomposite ceramic or glass material has a strain limit of about 2% or greater. In some embodiments, the nanocomposite ceramic or glass material has a strength of about $E/50$ or greater, wherein E is elastic modulus. In some embodiments, the nanocomposite ceramic or glass material has a strength of about $E/20$ or greater.

[0010] In another aspect, which may be combined with any other aspect of embodiment, the present disclosure relates to a method of forming a nanocomposite ceramic or glass material, comprising: (a) mixing: (i) raw matrix powder(s), (ii) nanostructure powder(s), fibers, platelets, or any combination thereof, and optionally (iii) one or more viscosity-reducing materials; (b) dispersing the matrix powder(s), nanostructure powder(s), fibers, platelets, or any combination thereof, and, optionally, the one or more viscosity-reducing materials in a solvent to form a nanostructure dispersion; (c) agitating the nanostructure dispersion to form a slurry; (d) drying the slurry to form a mixed powder; (e) melting the mixed powder; and (f) cooling the melted mixed powder to form the nanocomposite ceramic or glass material; wherein the nanostructure powder(s) comprises a core-shell nanostructure.

[0011] In some embodiments, the core-shell nanostructure comprises a core material and a shell material coating the core nanostructure; and the shell material improves the wettability of the nanostructure by the matrix material and/or dispersion of the nanostructure within the matrix, relative to the core nanostructure alone.

[0012] In some embodiments, the shell material comprises the same material as the matrix material. In some embodiments, the core nanostructure comprises a carbon-based material.

[0013] In some embodiments, in the nanocomposite ceramic or glass material, the nanostructure is present in the matrix material at a concentration (v/v) of at least about 1%. In some embodiments, the nanostructure is present in the matrix material at a concentration (v/v) of at least about 10%. In some embodiments, the nanostructure is present in the matrix material at a concentration (v/v) of at least about 20%.

[0014] In some embodiments, the nanocomposite ceramic or glass material has a fracture toughness of $2 \text{ MPa} \cdot \text{m}^{1/2}$ or greater. In some embodiments, the nanocomposite ceramic or glass material has a strain limit of about 2% or greater. In some embodiments, the nanocomposite ceramic or glass material has a strength of about $E/50$ or greater, wherein E is elastic modulus.

In some embodiments, the nanocomposite ceramic or glass material has a strength of about $E/20$ or greater.

DETAILED DESCRIPTION

[0015] In some embodiments, the present disclosure relates to ceramic matrix nanocomposites including a high volume fraction of uniformly dispersed nanostructures and to methods of manufacturing such nanocomposites. In some embodiments, a ceramic matrix nanocomposite comprises, consists essentially of, or consists of a matrix of one or more ceramics and reinforcing nanostructures dispersed in the matrix. In some embodiments, the reinforcing nanostructures comprise, consist essentially of, or consist of core-shell nanostructures.

Matrix Materials

[0016] In some embodiments, the matrix material may comprise any combination of glasses and/or ceramic materials. In some embodiments, the matrix material is amorphous or includes an amorphous phase. In some embodiments, the matrix material may comprise one or more glasses (e.g., silica, silicate glasses, fused silica glasses aluminosilicate glasses, borosilicate glasses, soda-lime glasses, lead glasses, quartz, phosphate glasses, germinates, tellurites, atimonates, arsenates, titanates, tantalates, fluoride glasses, doped glasses, or any combination thereof, etc.). By way of non-limiting example, suitable matrix materials include metal oxides (e.g., alkaline earth metal oxides, post-transition metal oxides, rare earth metal oxides, and transition metal oxides, such as aluminum oxide (Al_2O_3), magnesium oxide (MgO), titanium oxide (TiO_2), and zirconium oxide (ZrO_2)), non-metal oxides (e.g., metalloid oxides such as silicon oxide (SiO_2) and boron oxide (B_2O_3)), metal carbides (e.g., transition metal carbides, such as titanium carbide (TiC), niobium carbide (NbC), chromium carbide (Cr_3C_2), nickel carbide (NiC), hafnium carbide (HfC), vanadium carbide (VC), tungsten carbide (WC), and zirconium carbide (ZrC)), non-metal carbides (e.g., metalloid carbides such as silicon carbide (SiC)), metal silicides (e.g., transition metal silicides, such as titanium silicide (TiSi)), metal borides (e.g., transition metal borides, such as titanium boride (TiB_2), zirconium boride (ZrB_2), hafnium boride

(HfB₂), vanadium boride (VB₂), and tungsten boride (W₂B₅)), metal nitrides (e.g., transition metal nitrides), non-metal nitrides (e.g., metalloid nitrides such as silicon nitride), alloys, mixtures, or other combinations of two or more of the foregoing.

Nanostructure Materials

[0017] In some embodiments, nanostructures may have at least one dimension in a range of about 1 nm to about 1000 nm, such as about 1 nm to about 900 nm, about 1 nm to about 800 nm, about 1 nm to about 700 nm, about 1 nm to about 600 nm, about 1 nm to about 500 nm, about 1 nm to about 400 nm, about 1 nm to about 300 nm, about 1 nm to about 250 nm, about 1 nm to about 200 nm, about 1 nm to about 150 nm, about 1 nm to about 100 nm, about 1 nm to about 80 nm, about 1 nm to about 70 nm, about 1 nm to about 60 nm, about 1 nm to about 50 nm, about 1 nm to about 40 nm, about 1 nm to about 30 nm, about 1 nm to about 20 nm, about 1 nm to about 10 nm, about 1 nm to about 5 nm, or any range or value therein between. Of course, other ranges are contemplated, and the endpoints of any of the above ranges may be combined (e.g., about 25 nm to about 50 nm, about 300 nm to about 500 nm, about 100 nm to about 500 nm, and so forth).

[0018] In some embodiments, the nanostructures may have at least one average or median dimension (e.g., diameter, length, width, thickness, etc.) in a range of about 1 nm to about 1000 nm, such as about 1 nm to about 900 nm, about 1 nm to about 800 nm, about 1 nm to about 700 nm, about 1 nm to about 600 nm, about 1 nm to about 500 nm, about 1 nm to about 400 nm, about 1 nm to about 300 nm, about 1 nm to about 250 nm, about 1 nm to about 200 nm, about 1 nm to about 150 nm, about 1 nm to about 100 nm, about 1 nm to about 80 nm, about 1 nm to about 70 nm, about 1 nm to about 60 nm, about 1 nm to about 50 nm, about 1 nm to about 40 nm, about 1 nm to about 30 nm, about 1 nm to about 20 nm, about 1 nm to about 10 nm, about 1 nm to about 5 nm, or any range or value therein between. Of course, other ranges are contemplated, and the endpoints of any of the above ranges may be combined (e.g., about 25 nm to about 50 nm, about 300 nm to about 500 nm, about 100 nm to about 500 nm, and so forth).

[0019] In some embodiments, the nanostructures may comprise, consist essentially of, or consist of nanoparticles having an aspect ratio of about 1000 or less, about 900 or less, about 800 or less, about 700 or less, about 600 or less, about 500 or less, about 400 or less, about 300 or less, about 250 or less, about 200 or less, about 150 or less, about 100 or less, about 90 or less, about 80 or less, about 70 or less, about 60 or less, about 50 or less, about 40 or less, about 30 or less, about 25 or less, about 20 or less, about 15 or less, about 10 or less, about 9 or less, about 8 or less, about 7 or less, about 6 or less, about 5 or less, about 4 or less, about 3 or less, about 2.5 or less, about 2 or less, about 1.5 or less, about 1.2 or less, or any range or value therein between.

[0020] In some embodiments, the nanostructures may have generally spherical or spheroidal shapes, although other shapes and configurations of nanostructures are contemplated (*e.g.*, nanotubes, nanorods, nanocubes, nanoprisms, nanofibers, and nanoplatelets, or any combination thereof). In the case of nanoparticles of some embodiments, the nanoparticles can have at least one dimension (*e.g.*, an effective diameter which is twice an effective radius) or at least one average or median dimension (*e.g.*, an average effective diameter which is twice an average effective radius) in a range of in a range of about 1 nm to about 1000 nm, such as about 1 nm to about 900 nm, about 1 nm to about 800 nm, about 1 nm to about 700 nm, about 1 nm to about 600 nm, about 1 nm to about 500 nm, about 1 nm to about 400 nm, about 1 nm to about 300 nm, about 1 nm to about 250 nm, about 1 nm to about 200 nm, about 1 nm to about 150 nm, about 1 nm to about 100 nm, about 1 nm to about 80 nm, about 1 nm to about 70 nm, about 1 nm to about 60 nm, about 1 nm to about 50 nm, about 1 nm to about 40 nm, about 1 nm to about 30 nm, about 1 nm to about 20 nm, about 1 nm to about 10 nm, about 1 nm to about 5 nm, or any range or value therein between. Of course, other ranges are contemplated, and the endpoints of any of the above ranges may be combined (*e.g.*, about 25 nm to about 50 nm, about 300 nm to about 500 nm, about 100 nm to about 500 nm, and so forth).

[0021] In some embodiments, nanostructures may include one or more ceramics, although other nanostructure materials are contemplated. Examples of suitable nanostructure materials include metal oxides (*e.g.*, alkaline earth metal oxides, post-transition metal oxides, and transition metal

oxides, such as aluminum oxide (Al_2O_3), magnesium oxide (MgO), titanium oxide (TiO_2), and zirconium oxide (ZrO_2)), non-metal oxides (e.g., metalloid oxides such as silicon oxide (SiO_2)), metal carbides (e.g., transition metal carbides, such as titanium carbide (TiC), niobium carbide (NbC), chromium carbide (Cr_3C_2), nickel carbide (NiC), hafnium carbide (HfC), vanadium carbide (VC), tungsten carbide (WC), and zirconium carbide (ZrC)), non-metal carbides (e.g., metalloid carbides such as silicon carbide (SiC)), metal silicides (e.g., transition metal silicides, such as titanium silicide (TiSi)), metal borides (e.g., transition metal borides, such as titanium boride (TiB_2), zirconium boride (ZrB_2), hafnium boride (HfB_2), vanadium boride (VB_2), and tungsten boride (W_2B_5)), metal nitrides (e.g., transition metal nitrides), non-metal nitrides (e.g., metalloid nitrides such as silicon nitride), alloys, mixtures, or other combinations of two or more of the foregoing. Particular examples of suitable nanostructure materials include non-metal-containing ceramics, such as metalloid carbides and other metalloid-containing ceramics.

[0022] In some embodiments, nanostructures may include one or more carbon-based materials. By way of non-limiting example, suitable carbon-based materials may include carbon nanotubes, graphene, graphene oxide, graphite, diamond, amorphous carbon, fullerenes or any combination thereof.

Core-Shell Nanostructures

[0023] In some embodiments, the nanostructures may comprise core-shell nanostructures in which a core nanostructure (which may comprise any combination of the materials, in the sizes and/or shapes discussed above, at any of the dimensions discussed above) is coated with a shell of a second material (e.g., a shell material). In some embodiments, the shell may comprise any suitable material. For example, the shell material may comprise metal oxides (e.g., alkaline earth metal oxides, post-transition metal oxides, and transition metal oxides, such as aluminum oxide (Al_2O_3), magnesium oxide (MgO), titanium oxide (TiO_2), and zirconium oxide (ZrO_2)), non-metal oxides (e.g., metalloid oxides such as silicon oxide (SiO_2)), metal carbides (e.g., transition metal carbides, such as titanium carbide (TiC), niobium carbide (NbC), chromium carbide

(Cr₃C₂), nickel carbide (NiC), hafnium carbide (HfC), vanadium carbide (VC), tungsten carbide (WC), and zirconium carbide (ZrC)), non-metal carbides (e.g., metalloid carbides such as silicon carbide (SiC)), metal silicides (e.g., transition metal silicides, such as titanium silicide (TiSi)), metal borides (e.g., transition metal borides, such as titanium boride (TiB₂), zirconium boride (ZrB₂), hafnium boride (HfB₂), vanadium boride (VB₂), and tungsten boride (W₂B₅)), metal nitrides (e.g., transition metal nitrides), non-metal nitrides (e.g., metalloid nitrides such as silicon nitride), alloys, mixtures, or other combinations of two or more of the foregoing. In some embodiments, the shell may comprise an oxidized form of the material making up the core (e.g., graphene oxide on graphene). In some embodiments, the shell may comprise the same material(s) making up the matrix.

[0024] In some embodiments, the shell may be amorphous or comprise an amorphous phase. By way of non-limiting example, suitable shell materials include metal oxides (e.g., alkaline earth metal oxides, post-transition metal oxides, rare earth metal oxides, and transition metal oxides, such as aluminum oxide (Al₂O₃), magnesium oxide (MgO), titanium oxide (TiO₂), and zirconium oxide (ZrO₂)), non-metal oxides (e.g., metalloid oxides such as silicon oxide (SiO₂) and boron oxide (B₂O₃)), metal carbides (e.g., transition metal carbides, such as titanium carbide (TiC), niobium carbide (NbC), chromium carbide (Cr₃C₂), nickel carbide (NiC), hafnium carbide (HfC), vanadium carbide (VC), tungsten carbide (WC), and zirconium carbide (ZrC)), non-metal carbides (e.g., metalloid carbides such as silicon carbide (SiC)), metal silicides (e.g., transition metal silicides, such as titanium silicide (TiSi)), metal borides (e.g., transition metal borides, such as titanium boride (TiB₂), zirconium boride (ZrB₂), hafnium boride (HfB₂), vanadium boride (VB₂), and tungsten boride (W₂B₅)), metal nitrides (e.g., transition metal nitrides), non-metal nitrides (e.g., metalloid nitrides such as silicon nitride), alloys, mixtures, or other combinations of two or more of the foregoing.

[0025] In some embodiments, the shell material may include one or more carbon-based materials. By way of non-limiting example, suitable carbon-based materials may include carbon

nanotubes, graphene, graphene oxide, graphite, diamond, amorphous carbon, fullerenes, or any combination thereof.

{0026} In some embodiments, the shell may have an average thickness of more than one monolayer. In some embodiments, the shell may have an average thickness of less than one monolayer (*e.g.*, a partial monolayer). In some embodiments, the shell may have an average thickness of greater than or equal to about 0.1 monolayers, greater than or equal to about 0.2 monolayers, greater than or equal to about 0.3 monolayers, greater than or equal to about 0.4 monolayers, greater than or equal to about 0.5 monolayers, greater than or equal to about 0.6 monolayers, greater than or equal to about 0.7 monolayers, greater than or equal to about 0.8 monolayers, greater than or equal to about 0.9 monolayers, greater than or equal to about 1 monolayers, greater than or equal to about 1.2 monolayers, greater than or equal to about 1.5 monolayers, greater than or equal to about 1.8 monolayers, greater than or equal to about 2 monolayers, greater than or equal to about 2.5 monolayers, greater than or equal to about 3 monolayers, greater than or equal to about 3.5 monolayers, greater than or equal to about 4 monolayers, greater than or equal to about 4.5 monolayers, greater than or equal to about 5 monolayers, greater than or equal to about 6 monolayers, greater than or equal to about 7 monolayers, greater than or equal to about 8 monolayers, greater than or equal to about 9 monolayers, greater than or equal to about 10 monolayers, greater than or equal to about 11 monolayers, greater than or equal to about 12 monolayers, greater than or equal to about 13 monolayers, greater than or equal to about 14 monolayers, greater than or equal to about 15 monolayers, greater than or equal to about 20 monolayers, greater than or equal to about 25 monolayers, greater than or equal to about 30 monolayers, greater than or equal to about 35 monolayers, greater than or equal to about 40 monolayers, greater than or equal to about 45 monolayers, greater than or equal to about 50 monolayers, greater than or equal to about 60 monolayers, greater than or equal to about 70 monolayers, greater than or equal to about 80 monolayers, greater than or equal to about 90 monolayers, greater than or equal to about 100 monolayers, or more, or any range or value therein between.

[0027] In some embodiments, the shell may have an average thickness of greater than or equal to about 0.2 nm, greater than or equal to about 0.4 nm, greater than or equal to 0.5 nm, greater than or equal to about 0.6 nm, greater than or equal to about 0.8 nm, greater than or equal to about 1 nm, greater than or equal to about 1.2 nm, greater than or equal to about 1.4 nm, greater than or equal to about 1.5 nm, greater than or equal to about 1.6 nm, greater than or equal to about 1.8 nm, greater than or equal to about 2 nm, greater than or equal to about 2.5 nm, greater than or equal to about 3 nm, greater than or equal to about 3.5 nm, greater than or equal to about 4 nm, greater than or equal to about 4.5 nm, greater than or equal to about 5 nm, greater than or equal to about 6 nm, greater than or equal to about 7 nm, greater than or equal to about 8 nm, greater than or equal to about 9 nm, greater than or equal to about 10 nm, greater than or equal to about 15 nm, greater than or equal to about 20 nm, greater than or equal to about 25 nm, greater than or equal to about 30 nm, greater than or equal to about 35 nm, greater than or equal to about 40 nm, greater than or equal to about 45 nm, greater than or equal to about 50 nm, greater than or equal to about 60 nm, greater than or equal to about 70 nm, greater than or equal to about 80 nm, greater than or equal to about 90 nm, greater than or equal to about 100 nm, greater than or equal to about 150 nm, greater than or equal to about 200 nm, greater than or equal to about 250 nm, greater than or equal to about 300 nm, greater than or equal to about 350 nm, greater than or equal to about 400 nm, greater than or equal to about 450 nm, or greater than or equal to about 500 nm, or more, or any range or value therein between.

[0028] In some embodiments, the shell may cover the entire core or only partially cover the core. In some embodiments, the shell may cover the core at a ratio (by area) of greater than or equal to about 0.1%, greater than or equal to about 0.2%, greater than or equal to about 0.3%, greater than or equal to about 0.4%, greater than or equal to about 0.5%, greater than or equal to about 0.6%, greater than or equal to about 0.7%, greater than or equal to about 0.8%, greater than or equal to about 0.9%, greater than or equal to about 1%, greater than or equal to about 1.5%, greater than or equal to about 2%, greater than or equal to about 2.5%, greater than or equal to about 3%, greater than or equal to about 3.5%, greater than or equal to about 4%, greater than or equal to about 4.5%, greater than or equal to about 5%, greater than or equal to about 5.5%, greater than

or equal to about 6%, greater than or equal to about 6.5%, greater than or equal to about 7%, greater than or equal to about 7.5%, greater than or equal to about 8%, greater than or equal to about 8.5%, greater than or equal to about 9%, greater than or equal to about 9.5%, greater than or equal to about 10%, greater than or equal to about 15%, greater than or equal to about 20%, greater than or equal to about 25%, greater than or equal to about 30%, greater than or equal to about 35%, greater than or equal to about 40%, greater than or equal to about 45%, greater than or equal to about 50%, greater than or equal to about 55%, greater than or equal to about 60%, greater than or equal to about 65%, greater than or equal to about 70%, greater than or equal to about 75%, greater than or equal to about 80%, greater than or equal to about 85%, greater than or equal to about 90%, greater than or equal to about 95%, greater than or equal to about 96%, greater than or equal to about 97%, greater than or equal to about 98%, greater than or equal to about 99%, or about 100%, or any range or value therein between.

[0029] In some embodiments, the shell material may be formed on the core by any suitable method, including oxidative methods, physical vapor deposition, electrochemical deposition, chemical vapor deposition, or any other method suitable for forming the shell material on the core. In some embodiments, the oxidative methods may include thermal oxidation in an oxygen-containing atmosphere, oxidation in an ozone-containing atmosphere (*e.g.*, in UV-irradiated oxygen-containing gaseous environment), chemical oxidation (*e.g.*, using strong acids and/or oxidants, such as hydrogen peroxide), plasma treatment, or any other suitable method. In some embodiments, the shell may be deposited onto the core by physical vapor deposition (*e.g.*, sputtering). In some embodiments, the shell may be deposited onto the core by atomic layer deposition (ALD) or molecular layer deposition (MLD). In some embodiments, the shell may be formed on the core by wet chemical methods (*e.g.*, sol-gel).

Nanocomposite Formation and Properties

[0030] In some embodiments, the inclusion of nanostructures into the matrix material may enhance the mechanical, thermal, electronic, and/or optical properties of the matrix material. For

example SiC, carbon-based, or carbon-like materials may enhance the thermal properties of ceramic and/or glass matrix materials. By way of a further non-limiting example, certain borides (*e.g.*, TiB₂) may enhance the electrical properties of ceramic and/or glass matrix materials. By way of further non-limiting example, metal nanowires (*e.g.*, Au, Ag, Pt, Pd, Cu, etc.) may enhance thermal and electronic properties of glass and/or ceramic matrix materials. Those of ordinary skill in the art will recognize that there are other combinations of nanostructures and matrix materials to enhance one or more properties of the matrix materials.

[0031] In some embodiments, the nanostructures may have improved wettability in the matrix material and may be more readily dispersed into the matrix material. Suitable nanostructures can be selected for self-dispersion in a ceramic matrix for processing at a temperature T , which can be set to about $(T_{melt} + 200 \text{ K})$, with T_{melt} being a melting temperature of a matrix material, although other processing temperatures in a range greater than about T_{melt} and up to about $(T_{melt} + 250 \text{ K})$ are contemplated. In some embodiments, selection of the nanostructures can satisfy the following conditions: (1) the nanostructures undergo little or no chemical reaction with a melt of the matrix; (2) good wettability of the nanostructures by the melt of the matrix, as characterized by, for example, a contact angle θ of the melt with a respect to a surface of a nanostructure material at the processing temperature T of less than about 90° , such as about 88° or less, about 85° or less, about 80° or less, about 75° or less, about 70° or less, about 60° or less, about 50° or less, about 40° or less, or about 30° or less; and

$$|W_{vdwmax}| < kT \text{ or } [(A_{nanostructure})^{1/2} - (A_{matrix})^{1/2}]^2 \times (1/12) \times (R/d_l) < kT,$$

where $A_{nanostructure}$ is the Hamaker constant of the nanostructure material, A_{matrix} is the Hamaker constant of the matrix material, R is an average effective radius of the nanostructures, d_l can be set to be about 0.4 nm, and k is Boltzmann's constant.

[0032] In some embodiments, a ceramic matrix nanocomposite includes nanostructures at a high volume fraction of about 3% or greater, such as about 5% or greater, about 6% or greater, about 7% or greater, about 8% or greater, about 9% or greater, about 10% or greater, about 11% or

greater, about 12% or greater, about 13% or greater, about 14% or greater, about 15% or greater, about 20% or greater, about 25% or greater, or about 30% or greater, or about 35% or greater, or about 40% or greater, or about 45% or greater, or about 50% or greater, or any range or value therein between

[0033] During manufacturing of a ceramic matrix nanocomposite, a powder mixture is formed by combining one or more ceramics (such in a powder or particulate form, for example in the form of microstructures) and reinforcing nanostructures, followed by mixing, such as by a mechanical shaker or other manner of agitation and then dispersion in a solvent under ultrasonic processing and evaporation of the solvent. The nanostructures can be introduced into the well-blended powder mixture at a relatively high volume fraction of about 3% or greater, such as about 5% or greater, about 6% or greater, about 7% or greater, about 8% or greater, about 9% or greater, about 10% or greater, about 11% or greater, about 12% or greater, about 13% or greater, about 14% or greater, about 15% or greater, about 20% or greater, about 25% or greater, or about 30% or greater, about 35% or greater, about 40% or greater, about 45% or greater, and up to about 50% or greater.

[0034] The well-blended powder mixture is then heated to a temperature at or above a melting temperature of the one or more ceramics to form a melt under a protection gas of argon (Ar) or another inert gas. Agitation by ultrasonic processing and, in particular, ultrasonic cavitation-assisted processing can be performed on the melt during heating to reduce porosity and promote uniform dispersion of the nanostructures. A resulting nanocomposite is obtained by cooling under a protection gas of Ar or another inert gas. The resulting nanocomposite can provide desirable mechanical properties for various applications. For example, the nanocomposite can have a fracture toughness of about $2 \text{ MPa} \cdot \text{m}^{1/2}$ or greater, about $3 \text{ MPa} \cdot \text{m}^{1/2}$ or greater, about $4 \text{ MPa} \cdot \text{m}^{1/2}$ or greater, about $5 \text{ MPa} \cdot \text{m}^{1/2}$ or greater, or about $6 \text{ MPa} \cdot \text{m}^{1/2}$ or greater, and up to about $7 \text{ MPa} \cdot \text{m}^{1/2}$ or greater.

[0035] In some embodiments, the nanocomposite may have a strain limit of about 2% or greater, about 3% or greater, about 4% or greater, about 5% or greater, about 6% or greater, about 7% or greater, about 8% or greater, about 9% or greater, or about 10% or greater, and up to about 15% or greater. In some embodiments, the nanocomposite may have a strength of about $E/50$ or greater, about $E/45$ or greater, about $E/40$ or greater, about $E/35$ or greater, about $E/30$ or greater, about $E/25$ or greater, about $E/23$ or greater, about $E/20$ or greater, about $E/18$ or greater, about $E/16$ or greater, about $E/15$ or greater, about $E/14$ or greater, about $E/13$ or greater, about $E/12$ or greater, and up to about $E/11$ or greater, wherein E is elastic modulus.

[0036] In some embodiments, the present disclosure relates to a method of forming a nanocomposite ceramic material, comprising: (a) mixing: (i) raw matrix powder(s), (ii) nanostructure powder(s), and optionally (iii) one or more viscosity-reducing materials; (b) dispersing the matrix powder(s), nanostructure powder(s), and, optionally, the one or more viscosity-reducing materials in a solvent to form a nanostructure dispersion; (c) agitating the nanostructure dispersion to form a slurry; (d) drying the slurry to form a mixed powder; (e) melting the mixed powder; and (f) cooling the melted mixed powder to form the nanocomposite ceramic material.

[0037] In some embodiments, the nanostructures may be dispersed in the matrix material by a method comprising: (a) mixing raw matrix powder(s) and nanostructure powder(s)/fibers/platelets, such that the relative masses of matrix powder(s) and nanostructure powder(s) correspond to a volume percentage of nanostructures in the matrix material; (b) optionally adding one or more viscosity-reducing materials (*e.g.*, B_2O_3); (c) stirring the matrix powder(s), nanostructure powder(s), and the one or more viscosity-reducing materials; (d) dispersing the matrix powder(s), nanostructure powder(s), and the one or more viscosity-reducing materials in a solvent to form a nanostructure dispersion; (e) agitating the nanostructure dispersion to form a slurry; (f) drying the slurry to form a mixed powder; and (g) melting the mixed powder. Such methods are described, *e.g.*, in Q.-G. Jiang, *Strong and Tough Glass With*

Self-Dispersed Nanoparticles Via Solidification, 31 ADV. MATER. 1901803 (2019), the entirety of which is hereby incorporated by reference in its entirety.

[0038] As used herein, the singular terms “a,” “an,” and “the” may include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to an object may include multiple objects unless the context clearly dictates otherwise.

[0039] As used herein, the term “set” refers to a collection of one or more objects. Thus, for example, a set of objects can include a single object or multiple objects.

[0040] As used herein, the terms “connect,” “connected,” and “connection” refer to an operational coupling or linking. Connected objects can be directly coupled to one another or can be indirectly coupled to one another, such as via one or more other objects.

[0041] As used herein, the terms “substantially” and “about” are used to describe and account for small variations. When used in conjunction with an event or circumstance, the terms can refer to instances in which the event or circumstance occurs precisely as well as instances in which the event or circumstance occurs to a close approximation. When used in conjunction with a numerical value, the terms can refer to a range of variation of less than or equal to $\pm 10\%$ of that numerical value, such as less than or equal to $\pm 5\%$, less than or equal to $\pm 4\%$, less than or equal to $\pm 3\%$, less than or equal to $\pm 2\%$, less than or equal to $\pm 1\%$, less than or equal to $\pm 0.5\%$, less than or equal to $\pm 0.1\%$, or less than or equal to $\pm 0.05\%$. For example, a first numerical value can be “substantially” or “about” the same as or equal to a second numerical value if the first numerical value is within a range of variation of less than or equal to $\pm 10\%$ of the second numerical value, such as less than or equal to $\pm 5\%$, less than or equal to $\pm 4\%$, less than or equal to $\pm 3\%$, less than or equal to $\pm 2\%$, less than or equal to $\pm 1\%$, less than or equal to $\pm 0.5\%$, less than or equal to $\pm 0.1\%$, or less than or equal to $\pm 0.05\%$.

[0042] As used herein, the term “size” refers to a characteristic dimension of an object. Thus, for example, a size of an object that is spherical can refer to a diameter of the object. In the case of

an object that is non-spherical, a size of the non-spherical object can refer to a diameter of a corresponding spherical object, where the corresponding spherical object exhibits or has a particular set of derivable or measurable properties that are substantially the same as those of the non-spherical object. When referring to a set of objects as having a particular size, it is contemplated that the objects can have a distribution of sizes around the particular size. Thus, as used herein, a size of a set of objects can refer to a typical size of a distribution of sizes, such as an average size, a median size, or a peak size.

[0043] As used herein, the term “nanostructure” refers to an object that has at least one dimension in a range of about 1 nm to about 1000 nm. A nanostructure can have any of a wide variety of shapes, and can be formed of a wide variety of materials. Examples of nanostructures include nanofibers, nanoplatelets, and nanoparticles.

[0044] As used herein, the term “nanoparticle” refers to a nanostructure that is generally or substantially spherical or spheroidal. Typically, each dimension of a nanoparticle is in a range of about 1 nm to about 1000 nm, and the nanoparticle has an aspect ratio of about 5 or less, such as about 3 or less, about 2 or less, or about 1.

[0045] As used herein, the term “nanofiber” refers to an elongated nanostructure. Typically, a nanofiber has a lateral dimension (e.g., a width) in a range of about 1 nm to about 1000 nm, a longitudinal dimension (e.g., a length) in a range of about 1 nm to about 1000 nm or greater than about 1000 nm, and an aspect ratio that is greater than about 5, such as about 10 or greater.

[0046] As used herein, the term “nanoplatelet” refers to a planar-like, nanostructure.

[0047] As used herein, the term “microstructure” refers to an object that has at least one dimension in a range of about 1 μm to about 1000 μm . A microstructure can have any of a wide variety of shapes, and can be formed of a wide variety of materials. Examples of microstructures include microfibers, microplatelets, and microparticles.

[0048] Additionally, amounts, ratios, and other numerical values are sometimes presented herein in a range format. It is to be understood that such range format is used for convenience and brevity and should be understood flexibly to include numerical values explicitly specified as limits of a range, but also to include all individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly specified. For example, a ratio in the range of about 1 to about 200 should be understood to include the explicitly recited limits of about 1 and about 200, but also to include individual ratios such as about 2, about 3, and about 4, and sub-ranges such as about 10 to about 50, about 20 to about 100, and so forth.

[0049] While the disclosure has been described with reference to the specific embodiments thereof, it should be understood by those skilled in the art that various changes may be made and equivalents may be substituted without departing from the true spirit and scope of the disclosure as defined by the appended claim(s). In addition, many modifications may be made to adapt a particular situation, material, composition of matter, method, operation or operations, to the objective, spirit and scope of the disclosure. All such modifications are intended to be within the scope of the claim(s) appended hereto. In particular, while certain methods may have been described with reference to particular operations performed in a particular order, it will be understood that these operations may be combined, sub-divided, or re-ordered to form an equivalent method without departing from the teachings of the disclosure. Accordingly, unless specifically indicated herein, the order and grouping of the operations is not a limitation of the disclosure.

WHAT IS CLAIMED IS:

1. A nanocomposite ceramic or glass material, comprising:
one or more matrix materials; and
one or more nanostructures dispersed with the matrix material;
wherein the one or more nanostructures comprises a core-shell nanostructure.
2. The nanocomposite ceramic or glass material of claim 1, wherein:
the core-shell nanostructure comprises a core material and a shell material coating the core nanostructure; and
the shell material improves the wettability of the nanostructure by the matrix material and dispersion of the nanostructure within the matrix, relative to the core nanostructure alone.
3. The nanocomposite ceramic or glass material of claim 1 or 2, wherein the shell material comprises the same material as the matrix material.
4. The nanocomposite ceramic or glass material of any one of claims 1 to 3, wherein the core nanostructure comprises a carbon-based material.
5. The nanocomposite ceramic or glass material of any one of claims 1 to 4, wherein the nanostructure is present in the matrix material at a concentration (v/v) of at least about 1.0%.
6. The nanocomposite ceramic or glass material of any one of claims 1 to 5, wherein the nanostructure is present in the matrix material at a concentration (v/v) of at least about 10%.
7. The nanocomposite ceramic or glass material of any one of claims 1 to 6, wherein the nanocomposite ceramic or glass material has a fracture toughness of $2 \text{ MPa} \cdot \text{m}^{1/2}$ or greater.
8. The nanocomposite ceramic or glass material of any one of claims 1 to 7, wherein the nanocomposite ceramic or glass material has a strain limit of about 2% or greater.

9. The nanocomposite ceramic or glass material of any one of claims 1 to 9, wherein the nanocomposite ceramic or glass material has a strength of about $E/50$ or greater, wherein E is elastic modulus.

10. A method of forming a nanocomposite ceramic or glass material, comprising:

(a) mixing: (i) raw matrix powder(s), (ii) nanostructure powder(s), and optionally (iii) one or more viscosity-reducing materials;

(b) dispersing the raw matrix powder(s), nanostructure powder(s), and, optionally, the one or more viscosity-reducing materials in a solvent to form a nanostructure dispersion;

(c) agitating the nanostructure dispersion to form a slurry;

(d) drying the slurry to form a mixed powder;

(e) melting the mixed powder; and

(f) cooling the melted mixed powder to form the nanocomposite ceramic or glass material;

wherein the nanostructure powder(s) comprises a core-shell nanostructure.

11. The method of claim 10, wherein:

the core-shell nanostructure comprises a core material and a shell material coating the core nanostructure; and

the shell material improves the wettability of the nanostructure by the matrix material and/or dispersion of the nanostructure within the matrix, relative to the core nanostructure alone.

12. The method of claim 10 or claim 11, wherein the shell material comprises the same material as the matrix material.

13. The method of any one of claims 10 to 12, wherein the core nanostructure comprises a carbon-based material.

14. The method of any one of claims 10 to 13, wherein in the nanocomposite ceramic or glass material, the nanostructure is present in the matrix material at a concentration (v/v) of at least about 1%.
15. The method of any one of claims 10 to 14, wherein the nanostructure is present in the matrix material at a concentration (v/v) of at least about 10%.
16. The method of any one of claims 10 to 15, wherein the nanocomposite ceramic or glass material has a fracture toughness of $2 \text{ MPa} \cdot \text{m}^{1/2}$ or greater.
17. The method of any one of claims 10 to 16, wherein the nanocomposite ceramic or glass material has a strain limit of about 2% or greater.
18. The method of any one of claims 10 to 17, wherein the nanocomposite ceramic or glass material has a strength of about $E/50$ or greater, wherein E is elastic modulus.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US22/38584

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. B22F 5/10; B22C 15/24; B22F 1/00; B29C 43/36 (2022.01)

ADD. B29C 45/73; B29C 51/36 (2022.01)

CPC - INV. B22F 5/106; A61L 27/50; A61L 31/124; A61L 31/14; B22D 18/06; B22D 19/14; B22D 23/06

ADD. A61L 27/427; A61L 2400/12; C22C 32/0052

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)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — A	WO 2020/028643 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 06 February 2020; figure 10B; paragraphs [0059, 0086]	1-3 — 10-12
A	US 2011/0201984 A1 (DUBROW et al.) 18 August 2011; entire document	1-3, 10-12
A	WO 2017/173163 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 05 October 2017; entire document	1-3, 10-12

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“D” document cited by the applicant in the international application

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

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

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

07 October 2022 (07.10.2022)

Date of mailing of the international search report

DEC 02 2022

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

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Authorized officer

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US22/38584

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

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

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-9, 13-18
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.