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(54) Title: INTERFACE-CONTROLLED IN-SITU SYNTHESIS OF NANOSTRUCTURES IN MOLTEN METALS FOR MASS MANUFACTURING

(57) Abstract: Provided herein are manufacturing methods of a metal matrix nanocomposite, comprising: providing a molten metal including a first reactant; providing a molten salt, including a second set of reactants and a diluting salt, over a surface of the molten metal; and maintaining the molten salt and the molten metal at a temperature sufficient to react the first reactant and the second set of reactants, such that nanostructures with controlled small sizes are formed adjacent to an interface between the molten salt and the molten metal, and are incorporated into the molten metal for mass manufacturing of metal matrix nanocomposite.

INTERFACE-CONTROLLED IN-SITU SYNTHESIS OF NANOSTRUCTURES IN MOLTEN METALS FOR MASS MANUFACTURING

Cross-reference to related applications

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 62/833,096, filed April 12, 2019, which is incorporated by reference herein in its entirety.

Background

[0002] Metal matrix nanocomposites (MMNCs), exhibiting extraordinary properties, are highly demanded in the fields of aerospace, electronics and transportation, amongst others. It is also promising in additive manufacturing and welding. Other fabrication methods for MMNCs, such as ex-situ incorporation of pre-formed nanoparticles, have been constrained by the high cost of ex-situ nanoparticles. Nanoparticles with lower costs, such as Al_2O_3, are restricted for certain applications as nanocomposites incorporating such nanoparticles generally cannot be re-melted due to the poor wettability between a metal matrix and Al_2O_3 nanoparticles. Other methods involve in-situ synthesis of particles inside a matrix by volumetric reaction, which can be more cost effective than ex-situ methods, but are constrained by the production difficulty in obtaining small nanoparticles (such as less than about 50 nm) with narrow size distributions at high temperatures.

[0003] It is against this background that a need arose to develop the embodiments described herein.

Detailed Description

[0004] Embodiments of this disclosure are directed to an interface-controlled mechanism for nanostructure (e.g., nanoparticle) synthesis and incorporation into molten metals, and an improved and cost-effective method to manufacture in-situ MMNCs with large volume production capability. MMNCs enhanced by nanostructures exhibit higher strength and improved thermal stability over comparative alloys through Orowan strengthening, load bearing and Hall-Petch effects. Comparing to other methods to fabricate MMNCS, the improved method can effectively control a size of synthesized nanostructures at high temperatures through an interface reaction control mechanism.

[0005] Embodiments of this disclosure provide an effective mechanism of controlling the size of in-situ synthesized nanostructures into molten metals. In brief, reactants are placed in two immiscible liquids (e.g., molten salt and molten metal) and a reaction takes place at an interface between the two liquids to form nanostructures. By dilution of the reactants in the two liquids, the reaction is constrained to a region adjacent to the interface. By adjusting a reactant concentration (e.g., by dilution), reaction time and reaction temperature, a size of the resulting nanostructures can be well controlled with an unprecedented narrow distribution. A new theoretical model is developed to guide the fabrication of nanocomposites.

[0006] The improved method can be applied to various types of high-temperature material systems for various nanostructures. More specifically, the improved method has been applied to fabricate Al matrix/TiB_2 nanocomposites with TiB_2 nanoparticles that have an average size less than about 30 nm; Al matrix/TiC nanocomposites with TiC nanoparticles; Cu matrix/TiB_2 nanocomposites; and Cu matrix/WC/W_2C/W nanocomposites.

[0007] Aspects of some embodiments include the following:

Interface-controlled nanostructure synthesis mechanism in high temperature molten liquids

[0008] A reaction at an interface is used to control a size and a size distribution of synthesized nanostructures. For in-situ synthesis of nanostructures, after addition of one or more reactants into a first liquid and one or more other reactants into a second immiscible liquid, a reaction takes place at an interface between these two liquids and nanostructures will start to nucleate and grow. Due to the Brownian motion of the nanostructures, the nanostructures can leave the interface and stop growing. The size of the nanostructures can be controlled by adjusting their growth rate and growth time. The growth rate is determined by the supersaturation (dilution) and the diffusion rate of the reactants in the liquids. The growth time is a function of wettability between the nanostructures and the liquids, and temperature. Stirring and ultrasonication provide other approaches to tune the growth time at the interface, but generally does not tune the growth rate. The interface-controlled fabrication can be expanded from liquid-liquid systems to liquid-gas systems if certain reactants are gases.

Concentration-controlled (dilution) nanostructure size

[0009] Dilution can be used to control a size of synthesized nanostructures in high temperature liquids. The size of a growing particle r can be expressed as proportional to $[2DSt_g]^{1/2}$. Here, r is a radius of the particle; D is the diffusivity of reactants; S is supersaturation and is proportional to a concentration of the reactants; t_g is the growth time of the particle. Because the growth is controlled by the slowest step of the reaction, all of these parameters are for the slowest step of reaction. By dilution of the reactants in another liquid, the supersaturation can be well controlled. In brief, a lower concentration leads to a smaller size. As an example for in-situ TiB_2 nanoparticles in a high-temperature system of Al-K_2TiF_6-KBF_4, $KAlF_4$ is added as a diluting liquid into a molten salt, and it is found that an average size of TiB_2 is about 36 nm when the concentration of reactant KBF_4 is about 0.4 g/cm^3 in $KAlF_4$, while the average size increases to about 60 nm when the concentration increased to about 0.8 g/cm^3. The reaction temperature is set at about 900°C.

Temperature-controlled (diffusion coefficient) nanostructure size

[0010] The diffusion coefficient can be expressed by the following equation:

$$D = D_o\exp(-Q_D/kT)$$

[0011] Here, D_o is a constant, Q_D is an activation energy of diffusion, k is the Boltzmann constant, and T is temperature. Therefore, by lowering a reaction temperature, the diffusion coefficient can be reduced and a size of nanostructures can be reduced as well. As an example for in-situ TiB_2 nanoparticles in a high-temperature system of Al-K_2TiF_6-KBF_4 (with $KAlF_4$ dilution), an average size of TiB_2 is about 36 nm when the reaction temperature is about 900°C, and it can be further reduced to about 24.8 nm when the reaction temperature dropped to about 750°C. The concentration of KBF_4 in $KAlF_4$ is about 0.4 g/cm^3 in these cases.

Growth time-controlled nanostructure size

[0012] A time during which nanostructures remain near an interface can be reduced by agitation (e.g., stirring or ultrasonication). Agitation is optional and may be omitted for the fabrication of nanocomposites by an interface-controlled method for convenience of mass manufacturing.

Ultrahigh-volume percentage capacity

[0013] Nanostructures will cease to grow once the nanostructures leave a near-interface region. It is, therefore, possible to continuously form additional small nanoparticles at the interface. A high volume percentage is not practical for comparative methods due to the possibility of forming large particles. As an example, using an interface-controlled method, Al matrix/TiB_2 nanocomposites including about 30 vol.% of TiB_2 can be fabricated with an average size of about 36 nm and a narrow size distribution.

[0014] Advantages of embodiments of this disclosure include one or more of the following:

- Scalable manufacturing by casting to achieve casting of bulk MMNCs with small nanostructure size (e.g., an average size of about 50 nm or less, or about 30 nm or less) and a narrow size distribution.
- Relatively low cost.
- Applicable to different metal/nanostructure systems.
- Tunable nanostructure size.
- Tunable volume percentage of nanostructures.
- Allows omission of agitation.

Example Embodiments

[0015] In some embodiments, a manufacturing method of a metal matrix nanocomposite includes: (1) providing a molten metal including a first reactant; (2) providing a molten salt, including a second set of reactants, over a surface of the molten metal; and (3) maintaining the molten salt and the molten metal at a temperature sufficient to react the first reactant and the second set of reactants, such that nanostructures are formed adjacent to an interface between the molten salt and the molten metal, and are incorporated into the molten metal.

[0016] In some embodiments, providing the molten metal includes heating one or more metals to form the molten metal. Examples of suitable metals include aluminum (Al), magnesium (Mg), iron (Fe), silver (Ag), copper (Cu), manganese (Mn), nickel (Ni), titanium (Ti), chromium (Cr), cobalt (Co), and zinc (Zn). In some embodiments, the first reactant is a metal, such as Al. In some embodiments, the first reactant is a first metal, such as Al, and providing the molten metal includes heating the first metal and at least another different, second metal to form the molten metal. In some embodiments, the first reactant is an alloying element, such as silicon or other non-metal element.

[0017] In some embodiments, the second set of reactants includes a metal-containing salt. In some embodiments, the metal-containing salt is a metal-containing halide salt, such as metal-containing fluoride salt. In some embodiments, the second set of reactants also includes a boron-containing salt, such as a boron-containing halide salt (e.g., a boron-containing fluoride salt), a nitrogen-containing salt, or a silicon containing salt (e.g., a silicon-containing fluoride salt). In other embodiments, the second set of reactants also includes a carbon source, such as activated carbon, charcoal, or carbon black.

[0018] In some embodiments, the second set of reactants includes a metal-containing oxide. In some embodiments, the second set of reactants also includes a carbon source, such as activated carbon, charcoal, or carbon black.

[0019] In some embodiments, providing the molten salt includes combining the second set of reactants with a diluting salt. In some embodiments, the diluting salt is a halide salt, such as a fluoride salt or a chloride salt.

[0020] In some embodiments, the method further includes agitating the molten metal.

[0021] In some embodiments, the method further includes cooling the molten metal including the nanostructures incorporated therein to form the metal matrix nanocomposite.

[0022] In some embodiments, the nanostructures have an average size in a range of 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 200 nm, about 1 nm to about 100 nm, about 1 nm to about 70 nm, about 1 nm to about 50 nm, or about 1 nm to about 30 nm. In some embodiments, a distribution of sizes of the nanostructures is characterized by a standard deviation, relative to an average size, that is up to about 100%, up to about 90%, up to about 80%, up to about 70%, up to about 60%, or up to about 50% of the average size. In some embodiments, the nanostructures include nanoparticles having an aspect ratio of about 5 or less, or about 3 or less, or about 2 or less and having generally spherical or spheroidal shapes, although other shapes and configurations of nanostructures are contemplated, such as nanofibers and nanoplatelets.

[0023] In some embodiments, the metal matrix nanocomposite includes the nanostructures at a volume percentage in a range of about 0.5% or greater, about 1% or greater, about 2% or greater, about 3% or greater, 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 15% or greater, about 20% or greater, or about 25% or greater, and up to about 30% or greater.

[0024] In some embodiments, the method further includes subjecting the metal matrix nanocomposite to casting to form a metal part.

Examples

[0025] The following examples describe specific aspects of some embodiments of this disclosure to illustrate and provide a description for those of ordinary skill in the art. The examples should not be construed as limiting this disclosure, as the examples merely provide specific methodology useful in understanding and practicing some embodiments of this disclosure.

Example 1

[0026] In-situ synthesis of TiB_2 nanoparticles in Al matrix with average size below about 30 nm were synthesized.

[0027] In-situ synthesis of TiB_2 can be made through the following chemical reaction:

$$3K_2TiF_6 + 13Al = 3Al_3Ti + 3KAlF_4 + K_3AlF_6$$

$$2KBF_4 + 3Al = AlB_2 + 2KAlF_4$$

$$AlB_2 + Al_3Ti = TiB_2 + 4Al$$

[0028] Reactants for this reaction are K_2TiF_6, KBF_4 and Al. The two fluoride salts can be dissolved in $KAlF_4$ molten salt or other chloride molten salt such as KCl, NaCl or their mixture. The molten salt and molten Al are two immiscible liquids. The first two reactions will occur at the interface between the two liquids, and the TiB_2 nanoparticles will be formed in a region very close to the interface by the third reaction. The synthesis procedure is described as following.

[0029] Al is first melted in a graphite or alumina crucible by an induction furnace at a designated temperature from about 700°C to about 1100°C. A molten salt is then added on top of the Al melt. A certain amount of reactant salts is added into the molten salt. The amount of reactants is determined by the volume percentage of nanoparticles specified. The reaction will proceed for about 1 min to about 120 mins depending on the specified volume percentage. After reaction, the top molten salt will be poured out first, and the fabricated Al matrix TiB_2 nanocomposite will be subjected to casting or scraped out depending on the viscosity of the melt. It is found that if the volume percentage of the nanoparticles exceed about 6%, it may no longer be castable. Through the above synthesis, it is capable of fabricating nanocomposites including from about 0.5 vol.% to about 30 vol.% of TiB_2 nanoparticles. The average size of the TiB_2 nanoparticles can be controlled by the temperature and the concentration of the reactants in the molten salt. The smallest average size is about 24.8 nm and the largest average size is about 1 μm.

Example 2

[0030] In-situ synthesis of TiC nanoparticles in Al matrix with average size below about 100 nm were synthesized.

[0031] In-situ synthesis of TiC can be made through the following chemical reaction:

$$3K_2TiF_6 + 13Al = 3Al_3Ti + 3KAlF_4 + K_3AlF_6$$

$$3C + 4Al = Al_4C_3$$

$$Al_4C_3 + 3Al_3Ti = 3TiC + 13Al$$

[0032] Activated carbon, charcoal and carbon black can serve as carbon sources. The immiscible liquids are molten Al and molten $KAlF_4$. Both carbon source and K_2TiF_6 will be added into the molten salt. Dissolution of carbon in the salt is a criterion to obtain small TiC nanoparticles. Even though the solubility of carbon in the salt is small, the dissolution of carbon would avoid adding carbon directly into Al, which would result in large TiC particles. The synthesis procedure is described as following.

[0033] Al is first melted in a graphite or alumina crucible by an induction furnace at a designated temperature from about 850°C to about 900°C. Half of $KAlF_4$ is then added on top of the Al melt. The other half of the molten salt is mixed with reactants first and then added into the molten $KAlF_4$. Alternatively, $KAlF_4$ and the carbon source are mixed and melted at about 750°C for about 2 hrs and casted, and the casted mixture is then added into the molten salt. The amount of reactants is determined by the volume percentage of nanoparticles specified. The reaction will proceed for about 2 hrs to about 3 hrs depending on the specified volume percentage. After reaction, the top molten salt will be poured out first and the fabricated Al matrix/TiC nanocomposite will be subjected to casting or scraped out depending on the viscosity of the melt. The average size of the TiC nanoparticles is from about 100 nm to about 200 nm.

Example 3

[0034] In-situ synthesis of TiB_2 nanocomposites in Cu matrix were synthesized.

[0035] In-situ synthesis of TiB_2 in Cu can be achieved with the aid of Al as a reductant. Al is dissolved in molten Cu and Al will react with K_2TiF_6 and KBF_4, forming TiB_2. The detailed chemical reactions are the same as in-situ synthesis of TiB_2 nanoparticles in Al matrix. The residual Al in Cu matrix can be removed by a displacement reaction with a copper salt as shown below:

$$3Cu^{2+} + 2Al \rightarrow 3Cu + 2Al^{3+}$$

[0036] Reactants for this synthesis are K_2TiF_6, KBF_4, and Al. The two fluoride salts can be dissolved in molten $KAlF_4$ or other chloride molten salt such as KCl, NaCl or their mixture. The molten salts and molten Cu are two immiscible liquids. The chemical reactions will occur at the interface of the two liquids and the TiB_2 nanoparticles will be formed in a region very close to the interface. The synthesis procedure is described as following.

[0037] Cu is first melted in a graphite or alumina crucible by an induction furnace at about 1130°C. A certain amount of Al is then added to the molten Cu. $KAlF_4$ (or other chloride salt or mixture) is added on top of the molten Cu to form a molten salt. A mixture of a certain amount of reactant salts and $KAlF_4$ (or other chloride salt or mixture) is added into the molten salt. The amount of reactants is determined by the specified volume percentage of nanoparticles. Mechanical mixing by a graphite blade is applied. The reaction time will be from about 1 min to about 120 min depending on the specified volume percentage. To remove residual Al in Cu matrix, $CuCl_2$ (or CuF_2) can be added to the molten salt on top of the molten Cu directly after synthesis and held for about 5 min with mechanical mixing applied. $CuCl_2$ (or CuF_2) can also be added directly on top of a Cu/TiB_2 nanocomposite after the Cu/TiB_2 nanocomposite is re-melted to remove Al.

Example 4

[0038] In-situ synthesis of WC/W_2C/W nanocomposites in Cu matrix were synthesized.

[0039] In-situ synthesis of tungsten carbide nanoparticles in Cu can be achieved by the following reactions with the aid of Al as a reductant:

$$2Al + WO_3 = W + Al_2O_3$$

$$W + C = WC$$

[0040] WO_3 and carbon can partially dissolve in molten $KAlF_4$. Al is dissolved in molten Cu and Al will react with WO_3 and carbon, forming WC. Molten $KAlF_4$ and molten Cu are two immiscible liquids. The chemical reaction will occur at the interface between the two liquids. Formed WC will migrate into molten Cu eventually. The synthesis procedure is described as following.

[0041] The procedure is divided into two stages. First, to mitigate against floating of a carbon source (e.g., charcoal or activated carbon) in molten KAlF4, premixing of the carbon source, WO_3 and $KAlF_4$ is implemented. The carbon source is placed at the bottom of a graphite crucible and mixed $KAlF_4$ and micron-sized WO_3 particles are placed in the crucible, which is heated to about 750°C. The mixture is casted to form a solid mixture and it is then fragmented into small pieces for further reaction. Second, Cu is melted in a graphite or alumina crucible by an induction furnace at about 1130°C. A certain amount of Al is added to the molten Cu. $KAlF_4$ is subsequently added on top to form a molten salt. Solid pieces of premixed $KAlF_4$, carbon source, and WO_3 are added to the molten salt. The amount of reactants is determined by the specified volume percentage of nanoparticles. The reaction time will be about 120 min. X-ray diffraction (XRD) analysis of the final solidified Cu matrix nanocomposite shows that WC, W_2C and W are present in the Cu matrix.

[0042] 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.

[0043] 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.

[0044] 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.

[0045] 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 ±10% of that numerical value, such as less than or equal to ±5%, less than or equal to ±4%, less than or equal to ±3%, less than or equal to ±2%, less than or equal to ±1%, less than or equal to ±0.5%, less than or equal to ±0.1%, or less than or equal to ±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 ±10% of the second numerical value, such as less than or equal to ±5%, less than or equal to ±4%, less than or equal to ±3%, less than or equal to ±2%, less than or equal to ±1%, less than or equal to ±0.5%, less than or equal to ±0.1%, or less than or equal to ±0.05%.

[0046] 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 or spheroidal can refer to a diameter of the object. In the case of an object that is non-spherical or non-spheroidal, a size of the object can refer to a diameter of a corresponding spherical or spheroidal object, where the corresponding spherical or spheroidal object exhibits or has a particular set of derivable or measurable properties that are substantially the same as those of the non-spherical or non-spheroidal 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.

[0047] 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.

[0048] 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.

[0049] 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.

[0050] As used herein, the term “nanoplatelet” refers to a planar-like, nanostructure.

[0051] 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.

[0052] 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 are not a limitation of the disclosure.

What is claimed is:

1. A manufacturing method of a metal matrix nanocomposite, comprising:

providing a molten metal including a first reactant;

providing a molten salt, including a second set of reactants and a diluting salt, over a surface of the molten metal; and

maintaining the molten salt and the molten metal at a temperature sufficient to react the first reactant and the second set of reactants, such that nanostructures are formed adjacent to an interface between the molten salt and the molten metal, and are incorporated into the molten metal.

2. The manufacturing method of claim 1, wherein one or more of a concentration of the first reactant, a concentration of the second set of reactants, the temperature, and a time of reaction is set or adjusted according to a target size of the nanostructures.

3. The manufacturing method of claim 1, wherein the manufacturing method provides for mass production.

4. The manufacturing method of claim 1, wherein providing the molten metal includes heating one or more metals to form the molten metal.

5. The manufacturing method of claim 1, wherein the first reactant is a metal or an alloying element.

6. The manufacturing method of claim 1, wherein providing the molten metal includes heating the first reactant to form the molten metal.

7. The manufacturing method of claim 1, wherein the second set of reactants includes a metal-containing salt.

8. The manufacturing method of claim 7, wherein the metal-containing salt is a metal-containing halide salt.

9. The manufacturing method of claim 7 or claim 8, wherein the second set of reactants also includes a boron-containing salt.

10. The manufacturing method of claim 7 or claim 8, wherein the second set of reactants also includes a carbon source.

11. The manufacturing method of claim 7 or claim 8, wherein the second set of reactants also includes a silicon-containing salt.

12. The manufacturing method of claim 1, wherein the second set of reactants includes a metal-containing oxide.

13. The manufacturing method of claim 12, wherein the second set of reactants also includes a carbon source.

14. The manufacturing method of claim 1, wherein providing the molten salt includes combining the second set of reactants with the diluting salt.

15. The manufacturing method of claim 14, wherein the diluting salt includes a halide salt or a mixture of halide salts.

16. The manufacturing method of claim 14, wherein the diluting salt includes one or more chloride salts, one or more fluoride salts, or a mixture thereof.

17. The manufacturing method of claim 1, further comprising agitating the molten metal.

18. The manufacturing method of claim 1, further comprising cooling the molten metal including the nanostructures incorporated therein to form the metal matrix nanocomposite.

19. The manufacturing method of claim 18, wherein the nanostructures have an average size in a range of about 1 nm to about 500 nm.

20. The manufacturing method of claim 18, wherein a distribution of sizes of the nanostructures is characterized by a standard deviation, relative to an average size, that is up to about 50% of the average size.

21. The manufacturing method of claim 18, wherein the metal matrix nanocomposite includes the nanostructures at a volume percentage in a range of about 0.5% or greater and up to about 30%.

22. A metal matrix nanocomposite formed by the method of any one of claims 1-21.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US20/27775

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B22F 1/00; B82B 1/00, 3/00; C22C 21/06, 21/14, 21/16, 21/18 (2020.01)

CPC - B22F 1/0018; B82B 1/008, 3/0038, 3/0095; C22C 1/02, 1/10, 21/06, 21/14, 21/16, 21/18, 32/0036, 32/0047, 32/0052, 32/0073

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 data base consulted during the international search (name of data base 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 ---- Y	CN 108796251 A (MAITELI NEW MAT GUANGZHOU CO LTD) 13 November 2018 (machine translation English); abstract; claims 3-9; paragraphs [0021], [0023], [0027], [0042]-[0043], [0046], [0052]-[0053]	1-8, 9/7-8, 10/7-8, 12-19, 21 ---- 11/7-8, 20
Y	WO 2017/173163 A1 (THE REGENTS OF THE UNIVERSITY OF CALIFORNIA) 05 October 2017; paragraphs [0004], [0006], [0067], 0102], [0153], [0158]	11/7-8, 20

☐ 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 04 June 2020 (04.06.2020)	Date of mailing of the international search report 08 JUL 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US20/27775

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.: 22
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.