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(54) **OXIDATION AND CORROSION RESISTANT NANOSTRUCTURED COPPER-BASED METALLIC SYSTEMS**

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(57) **ABSTRACT**

Various embodiments are directed to oxidation- and/or corrosion-resistant nanostructured metallic system and techniques for producing such systems. The metallic system may include (i) a solvent of copper (Cu) metal that comprises 50 to 99.98 atomic percent (at. %) of the metallic system, (ii) a first solute of tantalum (Ta) metal dispersed in the solvent metal, the first solute comprising 0.01 to 50 at. % of the metallic system, (iii) a second solute of an oxidation and/or corrosion resistance-inducing metal dispersed in the solvent metal, the second solute comprising 0.01 to 50 at. % of the metallic system, and optionally (iv) a third solute of an additional metal dispersed in the solvent metal, the third solute comprising 0.01 to 50 at. % of the metallic system, the additional metal being an alkali metal, an alkaline earth metal, or a transition metal that is different from the solvent, first solute, and second solute.

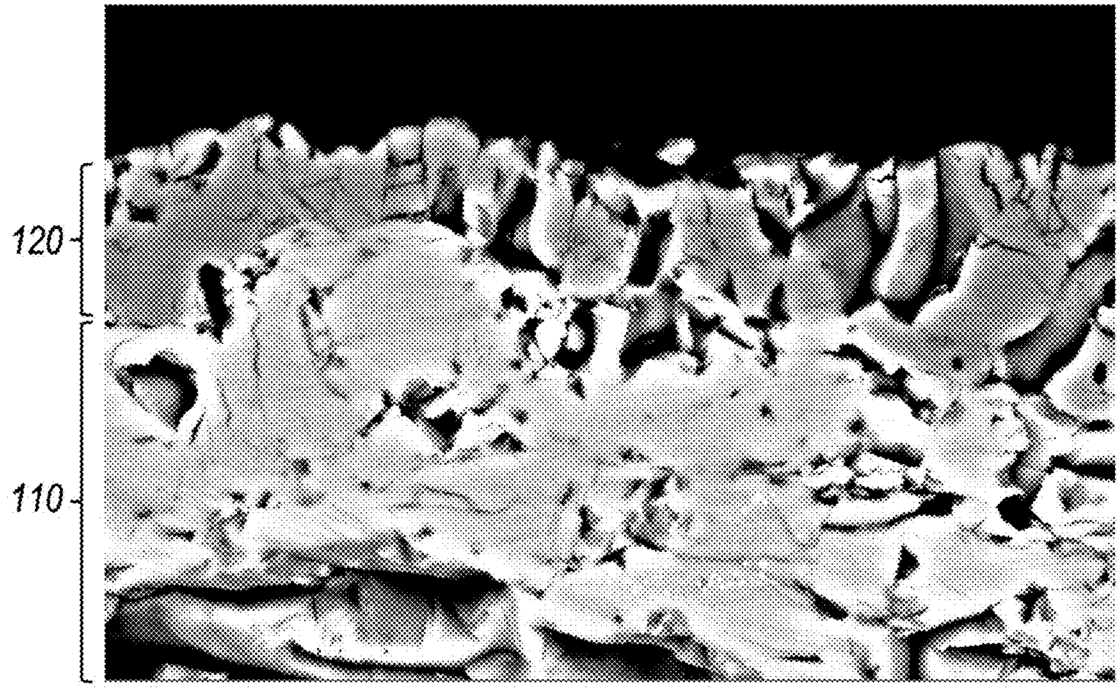

FIG. 1

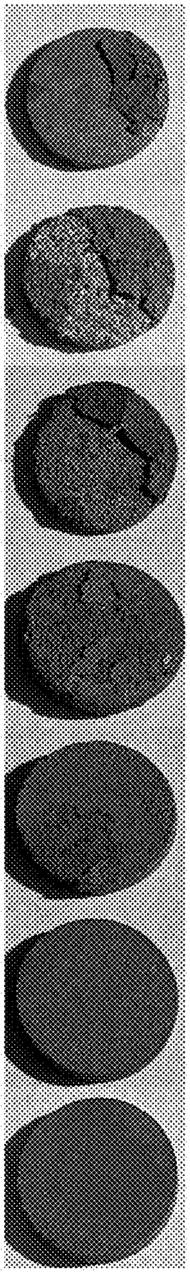

FIG. 2A

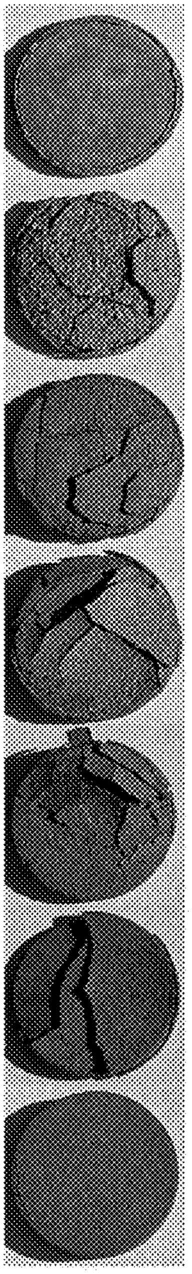

FIG. 2B

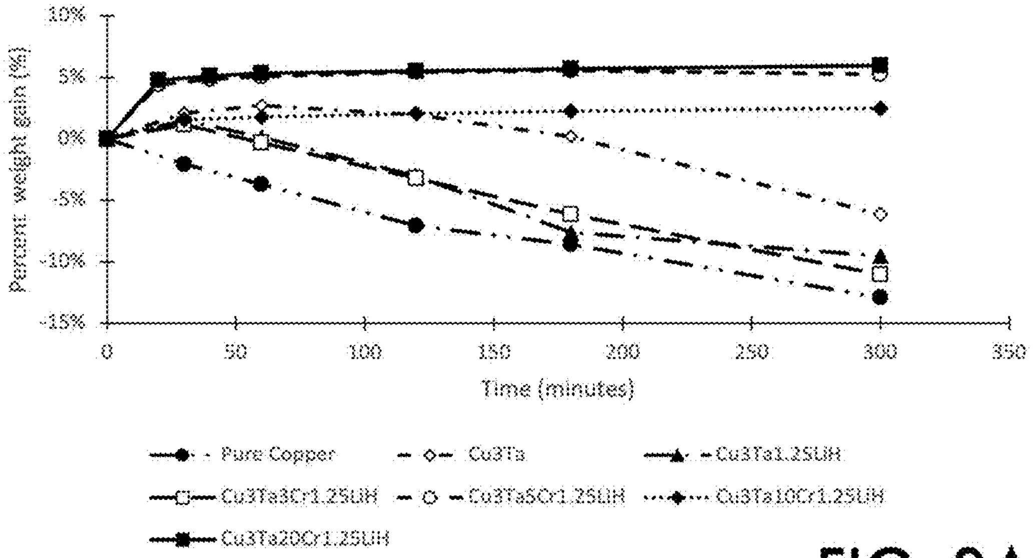
10%
5%
0%
-5%
-10%
-15%
Percent weight gain (%)
0
50
100
150
200
250
300
350
Time (minutes)
Pure Copper
Cu3Ta
Cu3Ta1.25LiH
Cu3Ta3Cr1.25LiH
Cu3Ta5Cr1.25LiH
Cu3Ta10Cr1.25LiH
Cu3Ta20Cr1.25LiH

FIG. 3A

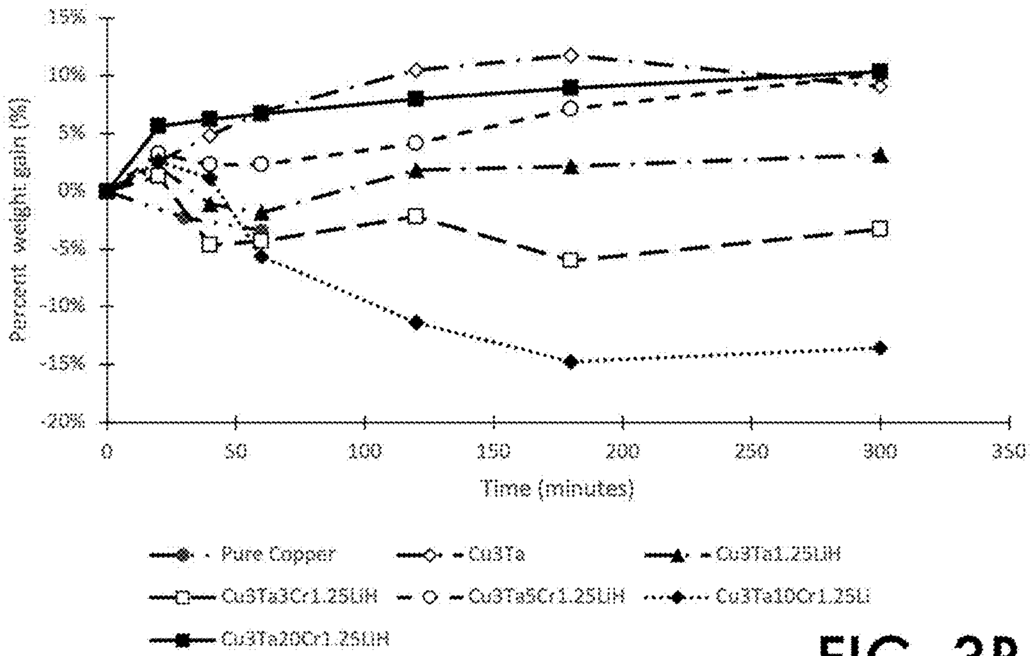
15%
10%
5%
0%
-5%
-10%
-15%
-20%
Percent weight gain (%)
0
50
100
150
200
250
300
350
Time (minutes)
Pure Copper
Cu3Ta
Cu3Ta1.25LiH
Cu3Ta3Cr1.25LiH
Cu3Ta5Cr1.25LiH
Cu3Ta10Cr1.25Li
Cu3Ta20Cr1.25LiH

FIG. 3B

# OXIDATION AND CORROSION RESISTANT NANOSTRUCTURED COPPER-BASED METALLIC SYSTEMS

## GOVERNMENT INTEREST

**[0001]** The invention described herein may be manufactured and used by or for the Government of the United States for all governmental purposes without the payment of any royalty.

## FIELD OF THE DISCLOSURE

**[0002]** The present disclosure relates to higher order oxidation- and/or corrosion-resistant nanostructured metallic copper (Cu)-based metallic systems, and in particular Cu-based metallic systems that incorporate an oxidation/corrosion resistant agent, such as chromium, into the system.

## BACKGROUND

**[0003]** This section is intended to introduce the reader to various aspects of art, which may be related to various aspects of the present invention that are described and/or claimed below. This discussion is believed to be helpful in providing the reader with background information to facilitate a better understanding of the various aspects of the present invention. Accordingly, it should be understood that these statements are to be read in this light, and not as admissions of prior art.

**[0004]** Bulk nanocrystalline metals, alloys, and composites have recently generated great interest and attention in the scientific community. This is mainly due to the exotic mechanical properties with which they are associated. Recent reports indicate that ultra-high strength and moderate ductility are possible in such metals. The combined possibility of ultra-high strength and ductility (i.e., ultra-tough nanocrystalline materials) make nanocrystalline metals and alloys the future of advanced metallurgy.

**[0005]** However, no such alloys available to date has been engineered to have high temperature oxidation/corrosion resistance. This major drawback severely limits their uses in real-world high temperature applications. "Real world" as used herein refers to ambient conditions in which the parts made from these alloys are exposed to an atmosphere in which oxidation/corrosion with the base metal can occur.

## BRIEF SUMMARY

**[0006]** Various deficiencies in the prior art are addressed below by the disclosed compositions of matter and techniques.

**[0007]** In some embodiments, an oxidation- and/or corrosion-resistant nanostructured metallic system may be provided. The metallic system may include alloys, and copper-immiscible alloys in particular. The metallic system may include (i) a solvent of copper (Cu) metal that comprises 50 to 99.98 atomic percent (at. %) of the metallic system, (ii) a first solute of tantalum (Ta) metal dispersed in the solvent metal, the first solute comprising 0.01 to 50 at. % of the metallic system, and (iii) a second solute of an oxidation and/or corrosion resistance-inducing metal dispersed in the solvent metal, the second solute comprising 0.01 to 50 at. % of the metallic system, and optionally (iv) a third solute of an additional metal dispersed in the solvent metal, the third solute comprising 0.01 to 50 at. % of the metallic system, the additional metal being a transition metal different from the solvent, first solute, and second solute. The metallic system may have an initial average grain size of no more than approximately 100 nm. The metallic system may be thermally stable, with the absence of substantial gross grain growth, such that the internal grain size of the solvent metal is substantially suppressed to no more than about 10 microns at approximately 98% of the melting point temperature of the solvent metal and the solute metal remains substantially uniformly dispersed in the solvent metal at that temperature.

**[0008]** In some embodiments, the additional metal(s) forming the third solute may be a group 4 element, a group 5 element, a group 6 element, Iron (Fe), cobalt (Co), Manganese (Mn), lithium (Li), or a combination thereof. In some embodiments, the oxidation and/or corrosion resistance-inducing metal forming the second solute may be chromium (Cr), zinc (Zn), aluminum (Al), nickel (Ni), titanium (Ti), halfnium (Hf), silver (Ag), or a combination thereof. In some embodiments, the second solute includes chromium (Cr). In some embodiments, the second solute may be 1 at. %-25 at. % of the metallic system.

**[0009]** In some embodiments, the metallic system is configured to form a coherent and non-permeable oxide layer comprising the second solute that prevents further oxidation of the metallic system when exposed to temperatures of at least 200° C. In some embodiments, the metallic system is configured to form a coherent and non-permeable oxide layer comprising the second solute that prevents further oxidation of the metallic system when exposed to temperatures of at least 500° C. In some embodiments, when exposed to an atmosphere containing a corrosive material, the metallic system is configured to form a coherent and non-permeable layer comprising the second solute that prevents further corrosion of the metallic system by the corrosive material.

**[0010]** In some embodiments, the metallic system is in bulk form and may include a pellet, bullet, ingot, bar, plate, disk, and/or sheet. In some embodiments, a high temperature machine part (such as a component of an engine or a turbine blade) may be provided that is formed of the high-density thermodynamically stable nanostructured metallic system disclosed herein.

**[0011]** In some embodiments, a process for forming a thermodynamically stable nanostructured copper-based metallic system as disclosed herein may be provided. The process may include subjecting powder metals of the solvent metal and the solute metals to a milling process using a milling device configured to shake or agitate the powder metals with ball media at some frequency which may be greater than 60 times per minute to impart impacts to its contents, and then consolidating the resultant powder metal subjected to the milling to form a bulk material. The bulk material may remain thermally stable, with the absence of substantial gross grain growth, such that the internal grain size of the solvent metal is substantially suppressed to no more than about 10 microns at approximately 98% of the melting point temperature of the solvent metal and the solute metals remain substantially uniformly dispersed in the solvent metal at that temperature.

**[0012]** Additional objects, advantages, and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0013]** The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the present invention and, together with a general description of the invention given above, and the detailed description of the embodiments given below, serve to explain the principles of the present invention.

**[0014]** FIG. **1** is a SEM image of a cross section of a Cu—Ta—Li-10Cr material after exposure to air at 800° C.

**[0015]** FIGS. **2**A and **2**B are images of 10 mm round discs, of different compositions, exposed to air at 700° C. (**1**A) and 900° C. (**1**B).

**[0016]** FIGS. **3**A and **3**B are graphs showing percent mass gained (or lost) for different compositions as a function of time at 700° C. (**2**A) and 900° C. (**2**B).

**[0017]** It should be understood that the appended drawings are not necessarily to scale, presenting a somewhat simplified representation of various features illustrative of the basic principles of the invention. The specific design features of the sequence of operations as disclosed herein, including, for example, specific dimensions, orientations, locations, and shapes of various illustrated components, will be determined in part by the particular intended application and use environment. Certain features of the illustrated embodiments have been enlarged or distorted relative to others to facilitate visualization and clear understanding. In particular, thin features may be thickened, for example, for clarity or illustration.

## DETAILED DESCRIPTION OF THE INVENTION

**[0018]** The following description and drawings merely illustrate the principles of the invention. It will thus be appreciated that those skilled in the art will be able to devise various arrangements that, although not explicitly described or shown herein, embody the principles of the invention and are included within its scope. Furthermore, all examples recited herein are principally intended expressly to be only for illustrative purposes to aid the reader in understanding the principles of the invention and the concepts contributed by the inventor(s) to furthering the art and are to be construed as being without limitation to such specifically recited examples and conditions. Additionally, the term, "or," as used herein, refers to a non-exclusive or, unless otherwise indicated (e.g., "or else" or "or in the alternative"). Also, the various embodiments described herein are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

**[0019]** The numerous innovative teachings of the present application will be described with particular reference to the presently preferred exemplary embodiments. However, it should be understood that this class of embodiments provides only a few examples of the many advantageous uses of the innovative teachings herein. In general, statements made in the specification of the present application do not necessarily limit any of the various claimed inventions. Moreover, some statements may apply to some inventive features but not to others. Those skilled in the art and informed by the teachings herein will realize that the invention is also applicable to various other technical areas or embodiments, such as seismology and data fusion.

**[0020]** Various embodiments are directed to oxidation and/or corrosion resistant nanostructured metallic systems.

**[0021]** Cu-based ternary systems may satisfy the generic formula, $Cu_aX_bY_c$, where copper is the solvent, the first solute metal is X and the second solute metal is Y. In the generic formula, a is preferably selected such that the solvent comprises 50 to 99.98 atomic percent (at. %) of the metallic system, and both b and c are preferably selected such that each solute, independently, comprises at least 0.01 at. %, or at least 0.1 at. %, up to 50 at. % of the metallic system.

**[0022]** The first solute metal (X) is preferably a transition metal, more preferably a group 4 element, a group 5 element, or a group 6 element, Iron (Fe), cobalt (Co), Manganese (Mn), and most preferably tantalum (Ta).

**[0023]** The second solute metal (Y) is an oxidation- and/or corrosion-resistance inducing agent. In some embodiments, the second solute metal is selected such that a density of the oxide formed by the metal is 2 g/cm$^3$ or greater, or 5 g/cm$^3$ or greater. In some embodiments, the second solute metal may be a transition metal or a post-transition metal. In some embodiments, the second solute metal may be chromium (Cr), zinc (Zn), aluminum (Al), nickel (Ni), titanium (Ti), hafnium (Hf), silver (Ag), or a combination thereof. In some embodiments, the second solute metal may be chromium.

**[0024]** Examples of such ternary systems include, e.g., 89Cu-5Ta-6Cr at. %, 88Cu-1.5Ta-10.5Cr at. %, or 90Cu-3Ta-7Hf at. %.

**[0025]** Depending on the specific composition, the metallic systems may have a crystalline to solid sol or emulsion-like sub-structure.

**[0026]** Cu-based quaternary systems may satisfy the generic formula, $Cu_aX_bY_cZ_d$, where copper is the solvent, the first solute metal is X, the second solute metal is Y, and the third solute metal is Z. In the generic formula, a is preferably selected such that the solvent comprises 50 to 99.98 atomic percent (at. %) of the metallic system, and b, c, and d are preferably selected such that each solute, independently, comprises at least 0.01 at. %, or at least 0.1 at. %, up to 50 at. % of the metallic system.

**[0027]** As with the ternary systems, the first solute metal (X) is preferably a transition metal, more preferably a group 4 element, a group 5 element, or a group 6 element, Iron (Fe), cobalt (Co), Manganese (Mn), and most preferably tantalum (Ta).

**[0028]** As with the ternary systems, the second solute metal (Y) is an oxidation and/or corrosion resistance agent. In some embodiments, the second solute metal may be selected such that a density of the oxide formed by the metal is 2 g/cm$^3$ or greater, or 5 g/cm$^3$ or greater. In some embodiments, the second solute metal may be a transition metal or a post-transition metal. In some embodiments, the second solute metal may be chromium (Cr), zinc (Zn), aluminum (Al), nickel (Ni), titanium (Ti), halfnium (Hf), silver (Ag), or a combination thereof. In some embodiments, the second solute metal may be chromium.

**[0029]** In some embodiments, the metallic systems may satisfy the generic formula, $Cu_aX_bY_c$, where b is 0.01-10 at. %, and c is 0.01-40 at. %. Depending on the specific composition, the metallic systems may have a crystalline to solid sol or emulsion-like sub-structure.

**[0030]** The third solute metal (Z) may be an additional material that may be an alkali metal, an alkaline earth metal, or a transition metal that is different from the solvent, first solute, and second solute. In some embodiments, the additional metal(s) forming the third solute may include a group 4 element, a group 5 element, a group 6 element, Iron (Fe), cobalt (Co), or a combination thereof.

**[0031]** Examples of such quaternary systems include, e.g., 86Cu-3Ta-5Fe-6Cr at. %, or 87Cu-1.5Ta-10Cr-1.5Li at. %.

**[0032]** The metallic system may have an initial average grain size of no more than approximately 100 nm. The metallic system may be thermally stable, with the absence of substantial gross grain growth, such that the internal grain size of the solvent metal is substantially suppressed to no more than about 10 microns at approximately 98% of the melting point temperature of the solvent metal and the solute metal remains substantially uniformly dispersed in the solvent metal at that temperature.

**[0033]** In some embodiments, the metallic system is configured to form a coherent and non-permeable oxide layer comprising the second solute that prevents further oxidation or corrosion of the metallic system when exposed to high temperatures and/or corrosive atmospheres.

**[0034]** In some embodiments, the metallic system is configured to form a coherent and non-permeable oxide layer comprising the second solute that prevents further oxidation of the metallic system when exposed to temperatures of at least 200° C. In some embodiments, the metallic system is configured to form a coherent and non-permeable oxide layer comprising the second solute that prevents further oxidation of the metallic system when exposed to temperatures of at least 500° C. In some embodiments, the metallic system is configured to form a coherent and non-permeable oxide layer comprising the second solute that prevents further oxidation of the metallic system when exposed to temperatures of at least 700° C. In some embodiments, the metallic system is configured to form a coherent and non-permeable oxide layer comprising the second solute that prevents further oxidation of the metallic system when exposed to temperatures of at least 900° C.

**[0035]** Referring to FIG. **1**, an image from an SEM shows an oxide layer **120** can be seen over the base metallic system **110**. The oxide layer is rich in the oxide- and/or corrosive-resistant agent. Specifically, in FIG. **1**, a Cu—Ta—Li-10Cr system was exposed to air at 800° C., and an oxide layer formed. EDS spot analysis indicated the oxide layer **120** was 48.71% O, 45.75% Cr, 5.37% Cu, and 0.17% Ta.

**[0036]** The improvement in oxidation and corrosion resistance can be seen visually. For example, as seen in FIGS. **2**A and **2**B, 10 mm round discs of various compositions were created and heated to 700° C. (**1**A) and 900 (**1**B). From top to bottom, the discs are: (i) pure Cu: (ii) Cu—Ta: (iii) Cu—Ta—Li: (iv) Cu—Ta—Li-3Cr: (v) Cu—Ta—Li-5Cr: (vi) Cu—Ta—Li-10Cr; and (vii) Cu—Ta—Li-20Cr.

**[0037]** As seen, at 700° C., discs (i)-(v) all showed oxide spalling, which can lead to part failure. The addition of even a small amount of chromium (e.g., discs (iv) and (v)) did show reduced oxidation and spalling effects. However, only discs (vi) and (vii), which had 10 and 20 at. % Cr added, respectively, showed none of the spalling seen in the other discs. At 900° C., only disc (vii) showed none of the spalling seen in other discs.

**[0038]** A similar pattern can be seen when exposing the material to a corrosive atmosphere (for example, a gas turbine blade exposed to air and sulfur dioxide).

**[0039]** Referring to FIGS. **3**A and **3**B, the percent mass gained (or lost) over time can be seen for various compositions exposed to air at 700° C. (**2**A) and 900° C. (**2**B) for compositions aligned with the ones in FIGS. **2**A and **2**B.

**[0040]** In some embodiments, the metallic system is in bulk form and may include a pellet, bullet, ingot, bar, plate, disk, and/or sheet. In some embodiments, a high temperature machine part (such as a component of an engine or a turbine blade) may be provided that is formed of the nanostructured metallic system disclosed herein.

**[0041]** To create such components, mechanical milling may be utilized. In general, mechanical milling/alloying produces nanostructured materials with grain sizes well below 100 nm by repeated mechanical attrition of coarser grained powdered materials. For example, precursor powders may be loaded into a steel vial and hardened steel or ceramic balls are also added. The vial then is sealed and shaken for extended periods of time. For example, the vials may be shaken 1060 times a minute resulting in some 2120 impacts a minute. This high-energy ball milling results in an almost complete breakdown of the initial structure of the particles.

**[0042]** More specifically, on an atomic level, atoms can be forced into a metastable random solid solution or potentially occupy defect sights such a dislocations, triple junctions, and grain boundaries. This process is critical for setting up thermodynamic stabilization. The breakdown occurs due to the collisions of the particles with the walls of the vial and the balls. The energy deposited by the impact of the milling balls is sufficient to displace the atoms from their crystallographic positions. On a microscopic level, the particles fracture, aggregate, weld, and re-fracture causing the evolution of a heavily worked substructure in the milled powers.

**[0043]** If more than one powder component is added into the vial, the components will be intimately mixed at an atomic level. As in mechanical alloying, this re-welding and re-fracturing continues until the elemental powders making up the initial charge are blended on the atomic level, such that either a solid solution and/or phase change results. The chemistry of the resulting alloy is comparable to the percentages of the initial elemental powders. With continued milling time, grain size reduction occurs, which eventually saturates at a minimum value that has been shown to scale inversely with melting temperature of the resultant compound. Of course, the process cycle can be interrupted to obtain intermediate grain size refinement of the powder blend and intermixing of its constituents.

## Example—Formation of Powder Metal Using High-Energy Milling

**[0044]** An exemplary alloyed Cu—Ta—Li—Cr compound was prepared by the inventors by loading high purity, 99.95% and 98.5%, respectively, ~325 mesh (approximately 45 μm) Cu, Ta, Li, and Cr powders with the correct weight ratios into a clean hardened steel vial to produce the desired atomic percent alloy. As an example, The Cu: Ta:Li:Cr ratio here was maintained at 86:3:10:1, with the expectation that the resultant alloy will be have a similar composition of Cu-3Ta-10Cr-1Li at. %.

**[0045]** Thirty-four (34) stainless steel (440C) ball-bearings, 17 of which having a diameter of ¼ inch and the other

17 having a diameter of ⅜ inch, were used as the milling media in a 8000D SPEX shaker mill. The 5-gram powder mass of copper and tantalum was milled with a 10:1 ball-to-powder mass (weight) ratio. Vials were sealed in (primarily) an Argon atmosphere (i.e., with $O_2<1$ ppm). This milling procedure results in a finely divided powder mass, consisting of particulates ranging from a few micro-to submillimeters. The interior structure of the particles is believed to likely consist of further structural refinement, specifically, grains or subgrains of Cu with individual Ta atoms to clusters of Ta atoms dispersed throughout.

**[0046]** The role of contaminants during the milling process can either have an additive or essentially inconsequential effect. On one hand, the latter case arises when a refractory milling medium is used, e.g., tungsten carbide (WC). The WC will fragment, but due to its chemical stability, it will be mostly unlikely that it will go into solution with the solvent. As such, it will more likely act as a finely dispersed kinetic pinning agent. On the other hand, a metallic milling medium, e.g., iron (Fe), can have beneficial or detrimental additive effects. Occasionally, incorporation of Fe is intentional, however, if not, the Fe contamination from milling in steel vial can be significantly reduced or completely mitigated by pre-coating the vial and milling media with pure Cu or the specified alloy to be milled prior to milling. Note, since WC vials are very brittle, this mitigation technique may not be as effective. Therefore, in general, steel vials are preferred over WC or other hard ceramic type vials and or milling media. Contamination should be maintained well less than 1% of the total mass of the metallic powder, and more preferably less than 0.5%.

**[0047]** During the high-energy milling process, the powder metal may be subjected to very low or a cryogenic temperature to embrittle the constituents. Cryogenic temperature is typically defined as temperature below about −150° C. Liquid nitrogen, for instance, having a temperature as low as −196° C. (77K), may be supplied to provide such cooling. Liquid nitrogen milling was made possible by placing the sealed vial in a thick nylon sleeve modified to allow placement into the high energy mill as well as to allow the in-flow and out-flow of liquid nitrogen. The vial was allowed to cool to liquid nitrogen temperature before starting the mill. Mechanical alloying at liquid nitrogen temperatures in the SPEX shaker mill for approximately 10 hours was performed until a minimization and saturation of the grain size occurred. This was verified using X-ray diffraction measurements. The purpose of using liquid nitrogen was to keep the powder cold such that it remained as brittle as possible, thereby preventing or, more precisely, reducing and minimizing the powder from adhering to the milling media and walls of the vial as well as maximizing the propensity to form saturated solid solutions. After the ball milling procedure was completed, the alloyed powder was removed from the steel vial in an Argon glove box and stored. Mechanical milling resulted in powders with a particle range of 20-200 μm. Other milling experiments were carried out using surfactants to prevent cold welding to the walls of the vial that yielded similar results to those done using liquid nitrogen.

**[0048]** In some embodiments, after generating the milled metals by exposing the powdered metal precursors to the high-energy milling process described previously, the method may include consolidating the milled metals (i.e., the resultant powder metal subjected to the high-energy milling) to form a bulk material. In some embodiments, the bulk material remains thermally stable, with the absence of substantial gross grain growth, such that the internal grain size of the solvent metals is substantially suppressed to no more than 10 microns, and preferably no more than about 250 nm at approximately 98% of the melting point temperature of the solvent metal and the solute metals remain substantially uniformly dispersed in the solvent metal at that temperature.

**[0049]** Bulk is defined as a structurally sound, fully-dense material. That is, the material is not in a loose, particulate, or powdered form. Additionally, the size of the article is sufficiently large enough, more than a few millimeters, such that conventional (i.e., not requiring specialized equipment or testing protocols) may be used to determine its mechanical properties, including yield strength, ultimate strength, or strain to failure. Typical bulk articles which can be formed include pellets, bullets, ingots, bars, plates, disks, or sheets.

**[0050]** Exemplary powdered metal compositions can be formed into bulk articles which retain their initial solid-sol or emulsion-like structure and properties. The disclosed metal powders lend themselves to various consolidation methods. These methods may include, e.g., pressure-less sintering, hot isostatic pressing, hot pressing, field assisted sintering (also known as spark plasma sintering), dynamic compaction using explosives or forging-like operations, high pressure torsion and extrusion methodologies including hot extrusion, cold extrusion, and equal channel angular extrusion. Special extrusion and consolidation procedures may further allow the modification of the initial isotropic nano-to micro-scale substructure of the composite to impart texture or spatial, location-dependent gradient to result in specific and/or directional properties.

**[0051]** Various embodiments enable composites with extraordinary properties to be fabricated in either the solid vapor or liquid states to create a solid-sol or emulsion-like substructure. The application of thermodynamic principles, combined with powder metallurgical methods is used.

**[0052]** In one example, mechanical alloying via high-energy milling, and a consolidation process, are used to fabricate Cu-rich composites for structural applications. This example entails a solid-solid embodiment which includes a prefabrication step of alloying the constituents into a finely divided, well-blended powder mixture, and, in turn, consolidating the powdered precursor with the appropriate metastable characteristics, into bulk, as will be described. This technique derives the composite from precursor elements remaining in the solid state.

**[0053]** After milling, the finely divided powder was then consolidated into a bulk sample using equal channel angular extrusion (ECAE). ECAE is a technique that entails the extrusion of a solid billet through a set of intersecting channels, essentially a right-angle corner machined into a tooling die. As the extrudate passes around the corner, it is subjected to a state of pure shear: approximately a strain of 1 is imparted to the extrudate in each extrusion or pass. The combination of hydrostatic and shear forces during the extrusion process causes the billet to densify. Multiple passes through the tooling die ensures complete densification. Change of the orientation of the billet between passes, imparts the billet with different grain morphologies and textures

**[0054]** Unlike solid materials, the consolidation of these powders cannot be easily performed directly. They need to be confined in a container or a can to ease densification and handling. Any engineering metal or alloy (e.g., pure Ni, pure Cu, Monel, or steel), that is close to the densified powder in strength, may serve for this function. Thus, for the consolidation of these powders, a cavity was first created in the solid billet. The cavity, typically cylindrical in shape, was then filled and packed with the nanostructured powder, evacuated (though, this is not always necessary), sealed, and extruded in the same manner as the solid billets, described previously. If desired, the billet and its contents can be heated to soften the powder mass prior to extrusion. Because of the extraordinary thermal properties of powders, retaining their metastable properties, treatment temperatures as high as 90-95% of the melting point of pure Cu could be used.

**[0055]** Various modifications may be made to the systems, methods, apparatus, mechanisms, techniques and portions thereof described herein with respect to the various figures, such modifications being contemplated as being within the scope of the invention. For example, while a specific order of steps or arrangement of functional elements is presented in the various embodiments described herein, various other orders/arrangements of steps or functional elements may be utilized within the context of the various embodiments. Further, while modifications to embodiments may be discussed individually, various embodiments may use multiple modifications contemporaneously or in sequence, compound modifications and the like.

**[0056]** Although various embodiments which incorporate the teachings of the present invention have been shown and described in detail herein, those skilled in the art can readily devise many other varied embodiments that still incorporate these teachings. Thus, while the foregoing is directed to various embodiments of the present invention, other and further embodiments of the invention may be devised without departing from the basic scope thereof. As such, the appropriate scope of the invention is to be determined according to the claims.

1. An oxidation- and/or corrosion-resistant nanostructured metallic system comprising:

a solvent of copper (Cu) metal that comprises 50 to 99.98 atomic percent (at. %) of the metallic system;

a first solute of tantalum (Ta) metal dispersed in the solvent metal, the first solute comprising 0.01 to 50 at. % of the metallic system;

a second solute of an oxidation and/or corrosion resistance-inducing metal dispersed in the solvent metal comprising chromium (Cr), zinc (Zn), nickel (Ni), titanium (Ti), halfnium (Hf), silver (Ag), or any combination thereof, the second solute comprising 0.01 to 50 at. % of the metallic system;

optionally, a third solute of an additional metal dispersed in the solvent metal, the third solute comprising 0.01 to 50 at. % of the metallic system, the additional metal being an alkali metal, an alkaline earth metal, or a transition metal that is different from the solvent, first solute, and second solute; and

wherein the metallic system has an initial average grain size of no more than approximately 100 nm;

wherein the metallic system is thermally stable, with an absence of substantial gross grain growth, such that an internal grain size of the solvent metal is substantially suppressed to no more than about 10 microns at approximately 98% of a melting point temperature of the solvent metal and the solute metal remains substantially uniformly dispersed in the solvent metal at that temperature.

**2**. The metallic system according to claim **1**, wherein the third solute is present in the metallic system and wherein the third solute metal is a group 4 element, a group 5 element, a group 6 element, Iron (Fe), cobalt (Co), Manganese (Mn), lithium (Li) or a combination thereof.

**3**. (canceled)

**4**. The metallic system according to claim **1**, wherein the oxidation and/or corrosion resistance-inducing metal consists of chromium (Cr).

**5**. The metallic system according to claim **4**, wherein the second solute comprises 1 at. %-20 at. % of the metallic system.

**6**. The metallic system according to claim **1**, wherein the metallic system is free of the third solute.

**7**. The metallic system according to claim **1**, wherein the metallic system is configured to form a coherent and non-permeable oxide layer comprising the second solute that prevents further oxidation of the metallic system when exposed to temperatures of at least 200° C.

**8**. The metallic system according to claim **1**, wherein the metallic system is configured to form a coherent and non-permeable oxide layer comprising the second solute that prevents further oxidation of the metallic system when exposed to temperatures of at least 500° C.

**9**. The metallic system according to claim **1**, wherein, when exposed to an atmosphere containing a corrosive material, the metallic system is configured to form a coherent and non-permeable layer comprising the second solute that prevents further corrosion of the metallic system by the corrosive material.

**10**. The metallic system according to claim **1**, wherein the metallic system is in bulk form and comprises: a pellet, bullet, ingot, bar, plate, disk, or sheet.

**11**. A high temperature machine part formed of a metallic system according to claim **1**.

**12**. The high temperature machine part according to claim **11**, wherein the machine part is a component of an engine or a turbine blade.

**13**. A process for forming an oxidation- and/or corrosion-resistant nanostructured copper-based metallic system, the metallic system comprising a solvent of copper (Cu) metal that comprises 50 to 99.98 atomic percent (at. %) of the metallic system, a first solute of tantalum (Ta) metal dispersed in the solvent metal, the first solute comprising 0.01 to 50 at. % of the metallic system, a second solute of an oxidation and/or corrosion resistance-inducing metal dispersed in the solvent metal comprising chromium (Cr), zinc (Zn), nickel (Ni), titanium (Ti), halfnium (Hf), silver (Ag), or any combination thereof, the second solute comprising 0.01 to 50 at. % of the metallic system, optionally a third solute of an additional metal dispersed in the solvent metal, the third solute comprising 0.01 to 50 at. % of the metallic system, the additional metal being an alkali metal, an alkaline earth metal, or a transition metal that is different from the solvent, first solute, and second solute, the process comprising:

generating milled metals by subjecting powder metals of the solvent metal and the solute metals to a milling process using a milling device configured to shake the powder metals with ball media in a generally back and forth direction at least 1060 times per minute to impart impacts to its contents; and

consolidating the milled metals to form a bulk material;

wherein the bulk material remains thermally stable, with an absence of substantial gross grain growth, such that an internal grain size of the solvent metal is substantially suppressed to no more than about 10 microns at approximately 98% of a melting point temperature of the solvent metal and the solute metals remain substantially uniformly dispersed in the solvent metal at that temperature.

**14**. The process according to claim **13**, wherein the third solute is present in the metallic system and wherein the third solute is a group 4 element, a group 5 element, a group 6 element, Iron (Fe), cobalt (Co), Manganese (Mn), lithium (Li) or a combination thereof.

**15**. (canceled)

**16**. The process according to claim **13**, wherein the second solute consists of chromium (Cr).

**17**. The process according to claim **13**, wherein the metallic system is free of the third solute.

**18**. The process according to claim **13**, wherein the second solute comprises 1 at. %-25 at. % of the metallic system.

**19**. The metallic system according to claim **1**, wherein the second solute metal is selected so that the density of the coherent and non-permeable oxide layer formed is 2 g/cm$^3$ or greater.

**20**. The metallic system according to claim **19**, wherein the second solute metal is selected so that the density of the coherent and non-permeable oxide layer formed is 5 g/cm$^3$ or greater.

**21**. The metallic system according to claim **1**, wherein the metallic system satisfies the formula, $Cu_aX_bY_c$, the first solute metal is X, the second solute metal is Y, a is 50 to 99.98 atomic percent (at. %) of the metallic system, and b is 0.01-10 at. %, and c is 0.01-40 at. %.

**22**. The metallic system according to claim **21**, wherein the metallic system comprises 89Cu-5Ta-6Cr at. %, 88Cu-1.5Ta-10.5Cr at. %, or 90Cu-3Ta-7Hf at. %.

**23**. The metallic system according to claim **1**, wherein the metallic system satisfies the formula, $Cu_aX_bY_cZ_d$, where the first solute metal is X, the second solute metal is Y, the third solute metal is Z, a is 50 to 99.98 atomic percent (at. %) of the metallic system, and b, c, and d are 0.1 at. %, to 50 at. % of the metallic system.

**24**. The metallic system according to claim **23**, wherein the metallic system comprises 86Cu-3Ta-5Fe-6Cr at. %, 87Cu-1.5Ta-10Cr-1.5Li at. % or Cu-3Ta-10Cr-1Li at. %.

**25**. The metallic system according to claim **1**, wherein the metallic system comprises Cu—Ta—Li-3Cr at. %, Cu—Ta—Li-5Cr at. %, Cu—Ta—Li-10Cr at. % or Cu—Ta—Li-20Cr. at. %.

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