

HOMOGENEOUS GRANULATED METAL BASED and METAL-CERAMIC BASED POWDERS

FIELD OF THE DISCLOSURE

[0001] The present disclosure generally relates to highly homogeneous metal based and metal-ceramic based powders and methods of making same, and, in particular, to metal based and metal-ceramic based powders utilized in consolidated form as sputtering targets for thin film deposition processes, e.g., as in manufacture of magnetic recording media, in powder form in other applications, e.g., plasma spray coating, and precursors for PM consolidation.

BACKGROUND OF THE DISCLOSURE

[0002] Metal based and metal-ceramic based powders and powder mixtures enjoy utility in a number of industrially useful applications, including use in consolidated form as sputtering targets for various thin film deposition processes, such as in the manufacture of thin film magnetic recording media, and in powder form in other coating applications, such as plasma spraying, and as precursors for PM consolidation, etc.

[0003] More specifically, the ever increasing demand for data storage requires higher areal recording density magnetic recording media than currently available. In this regard, efforts are continually made with the aim of increasing the areal recording density, i.e., bit density of the magnetic media. Conventional thin film thin-film type magnetic media, wherein a fine-grained polycrystalline magnetic alloy layer serves as the active recording layer, are generally classified as "longitudinal" or "perpendicular", depending upon the orientation of the magnetic domains of the grains of magnetic material.

[0004] Perpendicular recording media have been found to be superior to longitudinal media in achieving very high bit densities without experiencing the

thermal stability limit associated with the latter. In perpendicular magnetic recording media, residual magnetization is formed in a layer of a magnetic material in a direction ("easy axis") perpendicular to the surface of the layer.

[0005] In either instance, it is important that the magnetic grains of the recording layer be mutually separated, i.e., segregated, in order to physically and magnetically de-couple the grains and provide improved media performance characteristics. Segregation of the grains of magnetic media with Co-based alloy magnetic recording layers (e.g., CoCr alloys) can occur when oxides, nitrides, and/or carbides are present at the boundaries between adjacent magnetic grains to form so-called "granular" media. One currently practiced method for manufacturing such granular-type thin film magnetic recording media involves sputtering a target comprised of a ferromagnetic material (typically a Co-based alloy) and an oxide, nitride, or carbide material. The sputtering target is typically fabricated by consolidating a granular powder or powder mixture comprised of the magnetic metal or alloy and an oxide, nitride, or carbide material.

[0006] Uniform mixing of the component ("raw") powders prior to consolidation is critical for obtaining homogeneous sputtering targets, target performance, and, ultimately, performance of the resultant magnetic media. Typically, fine metal or metal alloy particles (i.e., 200 μm or less) and ultra-fine oxide, nitride, or carbide particles (i.e., 30 μm or less) are required as starting materials for forming products with fine grain sizes. However, homogeneous mixing of the ultra-fine oxide, nitride, or carbide particles in the metal or metal alloy matrix is a very challenging task. Specifically, if the fine oxide, nitride, or carbide particles agglomerate, or if the distribution of the ultra-fine oxide, nitride, or carbide particles on the surfaces of the fine metal or metal alloy particles is not homogeneous, poor performance of the resultant sputtering target results, including particle "spitting" leading to target cratering, non-uniform thin film formation, and degraded magnetic performance characteristics.

[0007] Current practice of the powder metallurgy industry is to utilize dry blending or grinding methodology for forming such sputtering targets via powder/granule consolidation techniques. However, such methodology is disadvantageous because of the tendency for agglomeration of cohesive fine particles and segregation of powders of different densities and/or particle sizes.

[0008] Accordingly, there exists a need for improved methodology for making high homogeneity granulated metal based and metal-ceramic based powders and powder mixtures useful as precursors in a number of industrially significant processes, including without limitation, thin film deposition processes such as dc, rf, and magnetically enhanced (magnetron) sputtering, cathode arc deposition, ion plating, as well as plasma spraying.

[0009] More specifically, there exists a need for improved methodology for making high homogeneity granulated metal powders comprising at least one magnetic metal element or an alloy thereof, e.g., CoCr, CoCrPt, CoPt, FePt, and at least one ceramic compound, such as an oxide, nitride, or carbide, or at least one non-metallic element. Suitable oxides include, for example, and without limitation: TiO_2 , SiO_2 , MgO , Ta_2O_5 , Nb_2O_5 , and Al_2O_3 ; suitable carbides include, for example, and without limitation: TaC and NbC; suitable nitrides include, for example, and without limitation: BN; and suitable non-metallic elements include, for example, and without limitation: B and C.

SUMMARY OF THE DISCLOSURE

[0010] An advantage of the present disclosure is improved methods of making homogeneous granulated metal based and metal-ceramic based powders.

[0011] Another advantage of the present disclosure is improved methods of making homogeneous granulated metal based and metal-ceramic based powders useful in the manufacture of sputtering targets, particularly magnetic sputtering targets.

[0012] Further advantages of the present disclosure include improved homogeneous granulated metal based and metal-ceramic based powders, particularly magnetic powders, and sputtering targets fabricated from the improved homogeneous granulated metal-based powders, particularly magnetic sputtering targets.

[0013] Additional advantages and features of the present disclosure will be set forth in the disclosure which follows and in part will become apparent to those having ordinary skill in the art upon examination of the following or may be learned from the practice of the present disclosure. The advantages may be realized and obtained as particularly pointed out in the appended claims.

[0014] According to an aspect of the present disclosure, the foregoing and other advantages are achieved in part by an improved method of making a homogeneous granulated metal based or metal-ceramic based powder, comprising steps of:

- (a) providing a preselected amount of at least one metal element or metal alloy and a preselected amount of at least one ceramic compound and/or at least one non-metallic element;

- (b) forming a homogeneous slurry/suspension or wet mixture comprising the preselected amounts of the at least one metal element or metal alloy and the at least one ceramic compound and/or the at least one non-metallic element, and a liquid phase comprising at least one liquid, at least one binder material, and at least one optional additive;

- (c) drying the slurry/suspension or mixture to remove at least a portion of the liquid phase and form a powder mixture comprising partially or completely dried granules; and

- (d) subjecting the partially or completely dried granules to a thermal de-binder process for effecting:

- (i) additional removal of any liquid phase, if present;
 - (ii) removal of the at least one binder material;

- (iii) reduction of carbon content;
- (iv) reduction of oxygen on the surfaces and/or interior of the metal constituent(s); and optional
- (v) partial sintering for strengthening of the particles for withstanding subsequent processing.

[0015] According to embodiments of the present disclosure, step (a) comprises providing a preselected amount of a powder containing the at least one metal element or metal alloy, a preselected amount of another powder containing the at least one ceramic compound, and/or a preselected amount of another powder containing the at least one non-metallic element.

[0016] In accordance with other embodiments of the present disclosure, step (a) comprises providing preselected amounts of a plurality of powders containing respective metal elements and/or metal alloys, respective ceramic compounds, and/or respective non-metallic elements. For example, according to certain embodiments of the present disclosure, step (a) comprises providing preselected amounts of two powders respectively containing first and second metal elements and/or alloys and/or preselected amounts of two powders respectively containing first and second ceramic compounds and/or non-metallic elements.

[0017] According to still other embodiments of the present disclosure, step (a) comprises providing a preselected amount of a compound of the metal or metal alloy and a preselected amount of a sol-gel of the ceramic compound or non-metallic element.

[0018] In accordance with embodiments of the present disclosure, step (a) comprises providing a preselected amount of at least one metal element or metal alloy comprising metal elements selected from the group consisting of: Co, Cr, Fe, Pt, Pd, Ru, Re, Ta, Al, Sm, Nd, etc., and a preselected amount of at least one ceramic compound and/or at least one non-metallic element selected from the group consisting of: TiO_2 , SiO_2 , MgO , Ta_2O_5 , Nb_2O_5 , Al_2O_3 , TaC, BN, ZrO_2 ,

HfO₂, ZnO, CaO, La₂O₃, WO₃, CoO, Co₂O₃, Y₂O₃, Cr₂O₃, MnO₂, NiO, CuO, CeO₂, Eu₂O₃, V₂O₅, Sm₂O₃, Sb₂O₅, BeO, BaO, B₂O₃, IrO₂, PbO, MoO₃, ReO₂, RuO₂, Ag₂O, SrO, TaC, NbC, BN, B, and C.

[0019] According to preferred embodiments of the present disclosure, step (a) comprises providing preselected amounts of a plurality of metal elements and/or metal alloys, ceramic compounds, and/or non-metallic elements selected from the above groups; and step (b) comprises forming the homogeneous slurry/suspension or wet mixture to comprise a liquid phase comprising at least one of water, an alcohol, and at least one organic solvent, and further comprising at least one inorganic or organic binder material.

[0020] Embodiments according to the present disclosure include those wherein step (b) comprises forming the homogeneous slurry/suspension or wet mixture to comprise a liquid phase comprising at least one of water, an alcohol, and at least one organic solvent selected from the group consisting of: acetone, toluene, alkanes such as hexane, heptane, xylene, decane, etc., and forming the homogeneous slurry/suspension or wet mixture to further comprise at least one organic binder material selected from the group consisting of: polyvinyl alcohol (PVA), polyethylene glycol (PEG), gum arabic, other natural gums, methyl cellulose, acrylic resin emulsions, ethylene oxide polymers, water soluble phenolics, alginates, natural or synthetic waxes, flour, starches, and inorganic binders such as carbonates, nitrides, oxylates, and oxychlorides. In addition, step (b) may comprise forming the homogeneous slurry/suspension or wet mixture to further comprise one or more of a deflocculating agent, wetting agent, de-foaming agent, plasticizer, and suspending agent.

[0021] Preferably, step (c) comprises spray drying, and step (d) comprises performing the thermal de-binder process to reduce the carbon content of the granules to less than about 500 ppm.

[0022] According to preferred embodiments of the present disclosure, step (d) comprises performing the thermal de-binder process in an atmosphere

comprising at least one reducing gas, e.g., selected from the group consisting of: H_2 , NH_3 , CO , forming gas, dissociated NH_3 , H_2/N_2 mixtures, and reformed hydrocarbon gases, and when an organic binder material is used, performing the thermal de-binder process in an atmosphere further comprising at least one weak oxidizing agent, e.g., selected from the group consisting of: H_2O , CO_2 , air, O_2 , and air or O_2 diluted in an inert gas or a non-oxidizing or weakly oxidizing gas.

[0023] According to another embodiment of the present disclosure, step (d) comprises performing the thermal de-binder process in an atmosphere comprising the at least one reducing gas only in a latter portion of the thermal de-binder process, and at the same or a different temperature than in an earlier portion of the process.

[0024] Another aspect of the present disclosure is homogeneous granulated metal based and metal-ceramic based powders formed by the above method, e.g., comprising at least one metal element or metal alloy comprising metal elements selected from the group consisting of: Co, Cr, Fe, Pt, Pd, Ru, Re, Ta, Al, Sm, and Nd and at least one ceramic compound or non-metallic element selected from the group consisting of: TiO_2 , SiO_2 , MgO , Ta_2O_5 , Nb_2O_5 , Al_2O_3 , TaC, BN, ZrO_2 , HfO_2 , ZnO , CaO , La_2O_3 , WO_3 , CoO , Co_2O_3 , Y_2O_3 , Cr_2O_3 , MnO_2 , NiO , CuO , CeO_2 , Eu_2O_3 , V_2O_5 , Sm_2O_3 , Sb_2O_5 , BeO , BaO , B_2O_3 , IrO_2 , PbO , MoO_3 , ReO_2 , RuO_2 , Ag_2O , SrO , TaC, NbC, BN, B, and C.

[0025] Yet another aspect of the present disclosure is magnetic sputtering targets fabricated from a homogeneous granulated metal based magnetic or metal-ceramic based powder formed by the above method.

[0026] Additional advantages of the present disclosure will become readily apparent to those skilled in this art from the following detailed description, wherein only the preferred embodiments of the present disclosure are shown and described, simply by way of illustration of the best mode contemplated for practicing the present disclosure. As will be realized, the disclosure is capable of other and different embodiments, and its several details are capable of

modification in various obvious respects, all without departing from the spirit of the present invention. Accordingly, the drawings and description are to be regarded as illustrative in nature, and not as restrictive.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0027] The present disclosure addresses and effectively solves, or at least mitigates, the above-described difficulties and drawbacks associated with conventional dry techniques for forming high homogeneity granulated metal based powders and metal-ceramic based powders and powder mixtures, thereby facilitating subsequent utilization of such powders in industrially significant applications, e.g., in consolidated form in thin film deposition processing and PM parts, and in granular form, e.g., as in plasma spraying.

[0028] Briefly stated, according to the present disclosure, wet processing is utilized to form a homogeneous slurry/suspension or a wet mixture of the constituent powders. Mixing of the particles at an individual particle level is achieved by proper mixing techniques and the addition of binder material(s) and other additives such as deflocculating agents, wetting agents, de-foaming agents, plasticizers, suspending agents, etc.

[0029] The homogeneous slurry/suspension is dried, e.g., as by spray drying, to remove the solvent. Because the slurry/suspension is dried very quickly, e.g., in about 2 – 20 sec.), the homogeneous mixing pattern obtained in the slurry is essentially maintained (preserved) upon drying. The particle size of the resultant granules can be in the range from about 10 to about 650 μm when formed by spray drying. Other methods for drying are applicable in the context of the present disclosure, and the particle sizes of the resultant particles can be larger or smaller, provided the homogeneous mixing pattern of the slurry/suspension is maintained (preserved) upon drying.

[0030] Alternatively, the constituent metal and ceramic and/or non-metallic compounds or elemental powders can be homogeneously mixed by

wetting the particle surfaces by addition thereto of a small amount of a suitable liquid solvent and binder material(s), e.g., at least one organic binder material, followed by drying of the well-mixed and wetted blend of powders to remove the solvent therefrom. The shape of the powder granules can be spherical, as when spray drying is utilized, or irregular.

[0031] In either instance, the slurry/suspension or wetted powder blend or mixture can be dried to cake or lump form and then crushed to yield appropriately small size particles or granules.

[0032] The binder material(s) is (are) then removed after drying via a thermal treatment, which thermal de-binder treatment lightly sinters the powder granules in order to maintain their integrity upon binder removal. Any oxygen absorbed or otherwise picked up by the granules during previous processing is reduced during the thermal de-binder treatment. However, oxides such as TiO_2 , SiO_2 , MgO , Ta_2O_5 , Nb_2O_5 , Al_2O_3 , etc., are unaffected at the temperatures utilized for the thermal de-binder treatment.

[0033] In this regard, a challenge typically encountered when organic binder materials or other additives are used in making the slurry/suspension or wetted powder is removal of the organic binder materials and additives from dried, granulated powders without the presence of air or O_2 as utilized in typical "binder burn-off", in order to avoid presence of a high amount of residual carbon from the organic binder materials and other additives. As a consequence, wet blending with addition of organic binder materials, followed by drying (e.g., spray drying) is rarely employed for granulation of high purity metal based and metal-ceramic based powders.

[0034] Further in this regard, another challenge encountered in granulation processing for making high purity metal based and metal-ceramic based powders is the tendency for surface oxidation of the metal particles to occur when water-based slurries/suspensions are processed and then dried in an air

atmosphere, resulting in significant oxygen incorporation ("pickup") in the metal-based phases.

[0035] In contrast with prior methodologies, the presently disclosed process is capable of producing high homogeneity granulated metal based and metal-ceramic based powders and powder mixtures without significant carbon content or oxygen pickup. A key feature of the presently disclosed process is subjecting partially or completely dried granules, formed as by spray drying, to a thermal de-binder process for effecting additional removal of any liquid phase (if required), removal of the at least one binder material, reduction of carbon content, reduction of oxygen on the surfaces of the metal constituent(s), and optionally partial sintering for strengthening of the granules for withstanding subsequent processing.

[0036] Further, the presently disclosed methodology can be employed for uniform mixing of multi-component powders or to coat/distribute one or more ultra-fine powders on the surfaces of other powders of equivalent or larger particle size.

[0037] Notable examples of the utility of the present disclosure include coating/distributing micron- or nano-sized non-metallic powder materials, e.g., oxides and ceramics, such as TiO_2 , SiO_2 , MgO , Ta_2O_5 , Nb_2O_5 , Al_2O_3 , TaC , BN , etc., on the surfaces of metal or metal alloy based particles, such as magnetic metals and powders of "master" alloys (via gas atomization or melting followed by crushing), including, for example but not limited to, Co , Cr , Pt , Fe , CoPt , CrCo , FePt , and CoCrPt to make high homogeneity granulated powders and powder mixtures with uniform distribution of the oxide or ceramic particles. The granulated powders afforded by the present disclosure may be consolidated and processed into targets suitable for thin film deposition processing, e.g., sputter deposition processing used in the manufacture of thin film magnetic recording media, including high areal recording density granular perpendicular media. In

addition, the methodology afforded by the present disclosure is useful in the fabrication of all manner of targets, etc., required for future applications.

[0038] For example, the present disclosure provides methodology for forming precursor granulated powders and powder mixtures suitable for forming sputtering targets to be used in fabricating the upcoming generation of granular perpendicular magnetic recording media, e.g., CoCrPt-TiO₂, CoCrPtSiO₂, and other CoCrPt-oxides. In addition, the methodology of the present disclosure is useful in preparing precursor granulated powders and powder mixture useful in fabricating sputtering targets contemplated for future generation thermally assisted perpendicular magnetic recording media, e.g., FePt-oxides and CoPt-oxides, where the oxides include, without limitation, TiO₂, SiO₂, MgO, Ta₂O₅, Nb₂O₅, and Al₂O₃. The present methodology is also useful in the preparation of precursor granulated powders or powder mixtures comprised of at least one metal and at least one ceramic material, including, for example and without limitation, carbides and nitrides such as TaC and BN. Other examples include CoPd oxides and Fe oxides.

[0039] The present methodology is also useful for making granulated precursor powders utilizing only a fraction of the requisite metal or metal alloy powders together with a fraction or all of the requisite ceramic, oxide, and/or non-metallic element powders. The resultant granulated powder is blended with the balance of requisite metal or metal alloy powders and ceramic, oxide, and/or non-metallic element powders for consolidation therewith.

[0040] The methodology afforded by the present disclosure will now be described in additional detail.

[0041] Mixing or blending of constituent powders is a critical step prior to consolidation for obtaining homogeneously composed solid materials. Dry blending or grinding processing for mixing or blending incur disadvantages such as agglomeration of the fine particles of the constituent powders which are naturally cohesive. Moreover, segregation in dry blending processing can be

worsened when the particle size distribution, density, and shapes of the constituent particles are different.

[0042] In this regard, powder particles having sizes less than about 20 – 30 μm are typically classified as "cohesive" in the powder processing industry. When particle sizes are in the micron or sub-micron range, they are more cohesive and easily agglomerate during dry mixing. Particle-level mixing is therefore not possible. However, the current trend in the magnetic data/information storage industry (i.e., manufacture of magnetic recording media) requiring sputtering targets with ever finer grain sizes (e.g., $< \sim 20 \mu\text{m}$) with high homogeneity poses significant problems to sputtering target manufacturers.

[0043] In a first step according to embodiments of the presently disclosed methodology, a wet mixing technique is utilized, employing either water, an alcohol, alcohol-water, or at least one organic solvent as the liquid phase. At least one binder material (inorganic or organic) is added and a homogeneous slurry/suspension of the constituent powders or a wetted homogeneous mixture of the constituent powders is formed. The choice of liquid phase material depends upon the desired microstructure of the ultimate product. For example, sputtering targets generally require an ultra-fine microstructure. Depending upon the final metal particle size and the chemical properties (e.g., reactivity) of the metal(s), compatibilities of the constituent powders with the solvents, either water, an alcohol, or at least one organic solvent, e.g., acetone, toluene, hexane, etc., is used for the liquid phase.

[0044] When ultra-fine microstructure is required (as with some types of sputtering targets), wet milling or grinding of the constituent ("raw") powders or coarse components can be employed for forming homogeneous slurries/suspensions. When super-fine microstructure is required (as in some types of sputtering targets), the metal powder(s) may be replaced with compound(s) containing the metal, e.g., an oxalate, carbonate, or hydroxide of the metal and the ceramic powder(s) replaced with a sol-gel to form a homogeneous

solution/suspension. In such instances, the metal compound(s) in the solvent is (are) either soluble or form a suspension comprising super-fine entities. After drying, the granulated mixture is subjected to thermal processing in a reducing atmosphere to decompose or reduce the metal-containing compounds to metal form.

[0045] In general, the raw powders may have a particle size distribution (PSD) ranging from a few nanometers (nm) to hundreds of microns, e.g., ~ 300 μm . The powder particles can be of any shape or density, and the resultant (mixed) compositions can vary over a wide range, depending upon the requirements of the intended target or alloy application.

[0046] Conventional inorganic or organic binders can be added to the slurry/suspension or wetted powder mixture, with 0.5 – 5 wt. % of the dry mixture being typical. However, $> \sim 5$ wt. % is also possible. Additives such as deflocculating agents, wetting agents, plasticizers, de-foaming agents, suspending agents, etc., can also be utilized for forming homogeneous solutions/suspensions.

[0047] The raw powders and binder material(s) are added to the at least one solvent (liquid phase) according to an optimized sequence, with appropriate mixing tools/devices (e.g., high shear mixers) being utilized for effecting homogeneous mixing of all of the ingredients. If finer particles sizes are required which are not available in raw powder form, a wet grinding or milling step in slurry/suspension form can be added to the process. The solids content of the slurry/suspension can be in the range from about 20 to about 80 wt. % when spray drying is the method of solvent removal. Alternatively, the wetted powder (where the solvent and at least one binder material only wet the surfaces of the particles) can have a solids content as high as about 99 wt. %.

[0048] In the next step according to the present methodology, the homogeneous slurry/suspension or wetted powder is dried to remove at least a portion of the liquid phase (i.e., solvent) and form a powder mixture comprising partially or completely dried granules. Any suitable drying technique can be

utilized for removing bulk solvent(s). Typically, the binder material(s) is (are) not removed during the drying step. However, when the temperature utilized for the drying step exceeds the thermal stability limit of the binder material, the binder material may be partially removed. The amount of remaining (i.e., residual) solvent can be controlled to be in a wide range as long as the dried powder maintains the homogeneous mixing achieved during the wet mixing step. Drying may comprise spray drying when the wet mix is in slurry/suspension form and the particle size of all powders present in the slurry/suspension is less than about 45 μm .

[0049] When organic solvent(s) is (are) used as the liquid phase, or when the metal particles after milling are highly flammable, an inert gas, e.g., N_2 , Ar, Ne, etc., should be used as the drying gas. In addition, a closed loop spray dryer is preferably employed when organic solvent(s) is (are) used as the liquid phase.

[0050] Following the drying step, the partially or completely dried powder is subjected to a thermal de-binder process for effecting additional removal of the liquid phase (if necessary), removal of the at least one binder material, reduction of carbon content, reduction of oxygen on the interior and/or exterior surfaces of the metal constituent(s), and optional partial sintering for strengthening of the granules for withstanding subsequent processing. In particular, when organic binder material(s) is (are) used in initial mixing processing of the constituent powders to form a slurry/suspension or wetted powder mixture, removal of the binder material(s) from the partially or completely dried powder is necessary to reduce the carbon content. Typically, the carbon content of the final granulated powder is expected to be less than about 1000, ppm, preferably less than about 500 ppm. The thermal de-binder process typically comprises heating the partially or completely dried powder at a temperature ranging from ambient to about 1400 $^{\circ}\text{C}$ for from about 30 min. to about 24 hrs., in an atmosphere comprising at least one strong reducing gas (e.g., H_2 , NH_3 , CO, dissociated NH_3 , H_2/N_2 mixtures, reformed hydrocarbon gases, etc.), to which at least one weak oxidizing agent

(H₂O, CO₂, etc.) is added. The weak oxidizing agent serves to selectively oxidize the organic binder agent(s) and any other carbon present in the partially or completely dried powder and convert them to gases which are readily removed from the solid material. The presence of the at least one strong reducing gas ensures that the metal(s) or metal alloy components of the partially dried powder is (are) not oxidized during the thermal treatment. When the partially dried powder contains an inorganic binder material, the thermal treatment may be conducted in an atmosphere comprising at least one reducing gas, in the absence of any weak oxidizing agent.

[0051] When water is utilized as the solvent for the liquid phase in forming the slurry/suspension or wetted powder, or air is used as a media for drying or present in the drying atmosphere, the outer and/or inner surface(s) of the metal constituent(s) of the powder may become oxidized. Therefore, another function of the thermal de-binder treatment is to reduce any oxygen present on the outer and/or inner surfaces of the metal particles. This may be accomplished during the thermal de-binder treatment (with the weak oxidizing agent present) or by switching to reducing gas(es) only at the latter portion of the treatment (in the absence of any weak oxidizing agent).

[0052] In addition to the above, the thermal de-binder treatment may serve to pre-sinter the particles, thereby increasing the strength of the granulated powder upon removal of the binder material(s). The extent of sintering is variable by appropriate regulation of the thermal de-binder treatment temperature.

[0053] The utility of the present disclosure will now be demonstrated with reference to the following illustrative, but non-limitative, examples.

[0054]

Example 1Co-15.56 wt. % TiO₂ granulated powder

A homogeneous slurry/suspension having the following composition was prepared.

Raw Co particle size: 1.4 – 8.5 μm

TiO₂ particle size: < 2 μm

Total solids (Co + TiO₂): 60 wt. %

Binders (dry basis): 1.5 wt. % polyvinyl alcohol (PVA)

1.5 wt. % polyethylene glycol (PEG)

Balance H₂O (solvent/liquid phase)

[0055]

The slurry/suspension was stirred/mixed to a homogeneous state and spray dried in a spray drier having a diameter of 20 ft. The slurry/suspension was constantly stirred during spray drying, with hot air employed as drying gas at an air inlet temperature of about 210 °C and air outlet temperature of about 110 °C. The moisture content after spray drying was about 0.2 wt. %. The spherical, spray dried particles were then thermally de-bindered/reduced in a muffle furnace for about 8 hrs. at a peak temperature of about 800 °C under a wet H₂ atmosphere. Any oxygen picked up by the metal constituent was reduced by switching to dry H₂ at a latter portion of the de-binder treatment conducted at about 800 °C for about 1 hr. The latter temperature is sufficient to reduce oxygen present on the surfaces of the metal particles but will not reduce the TiO₂. The thus-produced granulated powder contained spherically shaped particles with sizes ranging from about 15 to about 100 μm . The residual carbon in the final granulated powder was extremely low, as may be evident from the following:

Carbon content of the raw powder: 198 ppm

Carbon content of the spray-dried powder (containing binder): 15308 ppm

Carbon content after de-binder treatment: 87 ppm

[0056]

Example 2

Co-12.80 wt. % SiO₂ granulated powder

A homogeneous slurry/suspension having the following composition was prepared.

Raw Co particle size: 1.4 – 8.5 μm

SiO₂ particle size: < 5 μm

Total solids (Co + SiO₂): 50 wt. %

Binder (dry basis): 2 wt. % polyethylene glycol (PEG)

Balance H₂O (solvent/liquid phase)

[0057] The slurry/suspension was stirred/mixed to a homogeneous state and spray dried in a spray drier having a diameter of 20 ft. The slurry/suspension was constantly stirred during spray drying, with hot air employed as drying gas at an air inlet temperature of about 210 °C and air outlet temperature of about 110 °C. The moisture content after spray drying was about 0.3 wt. %. The spherical, spray dried particles were then thermally de-bindered/reduced in a muffle furnace for about 8 hrs. at a peak temperature of about 800 °C under a wet H₂ atmosphere. Any oxygen picked up by the metal constituent was reduced by switching to dry H₂ at a latter portion of the de-binder treatment conducted at about 800 °C for about 1 hr. The latter temperature is sufficient to reduce oxygen present on the surfaces of the metal particles but will not reduce the SiO₂. The thus-produced granulated powder contained spherically shaped particles with sizes ranging from about 15 to about 150 μm . The residual carbon in the final granulated powder was extremely low, as may be evident from the following:

Carbon content of the raw powder: 206 ppm

Carbon content of the spray-dried powder (containing binder): 11216 ppm

Carbon content after de-binder treatment: 72 ppm

[0058]

Example 3Fe-15.31 wt. % SiO₂ granulated powder

A homogeneous slurry/suspension having the following composition was prepared.

Raw Fe particle size: 3 – 12 μm

SiO₂ particle size: < 5 μm

Total solids (Co + SiO₂): 67 wt. %

Binder (dry basis): 3 wt. % polyethylene glycol (PEG)

Balance H₂O (solvent/liquid phase)

[0059]

The slurry/suspension was stirred/mixed to a homogeneous state and spray dried in a spray drier having a diameter of 20 ft. The slurry/suspension was constantly stirred during spray drying, with hot air employed as drying gas at an air inlet temperature of about 210 °C and air outlet temperature of about 110 °C. The moisture content after spray drying was about 0.2 wt. %. The spherical, spray dried particles were then thermally de-bindered/reduced in a muffle furnace for about 9 hrs. at a peak temperature of about 700 °C under a wet H₂ atmosphere. Any oxygen picked up by the metal constituent was reduced by switching to dry H₂ at a latter portion of the de-binder treatment conducted at about 700 °C for about 1 hr. The latter temperature is sufficient to reduce oxygen present on the surfaces of the metal particles but will not reduce the SiO₂. The thus-produced granulated powder contained spherically shaped particles with sizes ranging from about 15 to about 120 μm . The residual carbon in the final granulated powder was extremely low, as may be evident from the following:

Carbon content of the raw powder: 276 ppm

Carbon content of the spray-dried powder (containing binder): 14530 ppm

Carbon content after de-binder treatment: 40 ppm

[0060]

Example 4Co-14.31 wt. % Cr-13.50 wt. % TiO₂ granulated powder

A homogeneous slurry/suspension having the following composition was prepared.

Raw Co particle size: 1.4 – 8.5 μm

Raw Cr particle size: < 37 μm

TiO₂ particle size: < 2 μm

Total solids (Co + Cr + SiO₂): 62 wt. %

Binder (dry basis): 1.4 wt. % polyvinyl alcohol (PVA)

1.4 wt. % polyethylene glycol (PEG)

Balance H₂O (solvent/liquid phase)

[0061]

The slurry/suspension was stirred/mixed to a homogeneous state and spray dried in a spray drier having a diameter of 20 ft. The slurry/suspension was constantly stirred during spray drying, with hot air employed as drying gas at an air inlet temperature of about 210 °C and air outlet temperature of about 110 °C. The moisture content after spray drying was about 0.2 wt. %. The spherical, spray dried particles were then thermally de-bindered/reduced in a muffle furnace for about 8 hrs. at a peak temperature of about 900 °C under a wet H₂ atmosphere. Any oxygen picked up by the metal constituent was reduced by switching to dry H₂ at a latter portion of the de-binder treatment conducted at about 900 °C for about 1 hr. The latter temperature is sufficient to reduce oxygen present on the surfaces of the metal particles but will not reduce the TiO₂. The thus-produced granulated powder contained spherically shaped particles with sizes ranging from about 15 to about 180 μm . The residual carbon in the final granulated powder was extremely low, as may be evident from the following:

Carbon content of the raw powder: 202 ppm

Carbon content of the spray-dried powder (containing binder): 12916 ppm

Carbon content after de-binder treatment: 110 ppm

[0062]

Example 5

Co-8.37 wt. % Cr-20.68 wt. % Fe-10.28 wt. % TiO₂ granulated powder

A homogeneous slurry/suspension having the following composition was prepared.

Raw Co particle size: < 7 μm

Raw Cr particle size: < 20 μm

Raw Fe particle size: < 12 μm

TiO₂ particle size: < 2 μm

Total solids (Co + Cr + Fe + TiO₂): 68 wt. %

Binder (dry basis): 1.5 wt. % polyvinyl alcohol (PVA)

1.5 wt. % polyethylene glycol (PEG)

Deflocculating agent: Darvan C[®] - 0.5 wt. %

De-foaming agent: Foam Blaster-327[®] - 0.02 wt %

Balance H₂O (solvent/liquid phase)

[0063] The slurry/suspension was stirred/mixed to a homogeneous state and spray dried in a spray drier having a diameter of 20 ft. The slurry/suspension was constantly stirred during spray drying, with hot air employed as drying gas at an air inlet temperature of about 210 °C and air outlet temperature of about 110 °C. The moisture content after spray drying was about 0.2 wt. %. The spherical, spray dried particles were then thermally de-bindered/reduced in a muffle furnace for about 9 hrs. at a peak temperature of about 750 °C under a wet H₂ atmosphere. Any oxygen picked up by the metal constituent was reduced by switching to dry H₂ at a latter portion of the de-binder treatment conducted at about 750 °C for about 1 hr. The latter temperature is sufficient to reduce oxygen present on the surfaces of the metal particles but will not reduce the TiO₂. The thus-produced granulated powder contained spherically shaped particles with sizes ranging from about 15 to about 160 μm . The residual carbon in the final granulated powder was extremely low, i.e., 98 ppm.

[0064]

Example 6Co-7.88 wt. % Cr-25.25 wt. % Mo-9.69 wt. % TiO₂ granulated powder

A homogeneous slurry/suspension having the following composition was prepared.

Raw Co particle size: $< 7 \mu\text{m}$

Raw Cr particle size: $< 15 \mu\text{m}$

Raw Mo particle size: $< 10 \mu\text{m}$

TiO₂ particle size: $< 2 \mu\text{m}$

Total solids (Co + Cr + Mo + TiO₂): 67 wt. %

Binder (dry basis): 2 wt. % polyvinyl alcohol (PVA)

1 wt. % polyethylene glycol (PEG)

Deflocculating agent: Darvan C® - 0.3 wt. %

De-foaming agent: Foam Blaster-327® - 0.02 wt %

Balance H₂O (solvent/liquid phase)

[0065] The slurry/suspension was stirred/mixed to a homogeneous state and spray dried in a spray drier having a diameter of 20 ft. The slurry/suspension was constantly stirred during spray drying, with hot air employed as drying gas at an air inlet temperature of about 210 °C and air outlet temperature of about 110 °C. The moisture content after spray drying was about 0.2 wt. %. The spherical, spray dried particles were then thermally de-bindered/reduced in a muffle furnace for about 9 hrs. at a peak temperature of about 750 °C under a wet H₂ atmosphere. Any oxygen picked up by the metal constituent was reduced by switching to dry H₂ at a latter portion of the de-binder treatment conducted at about 900 °C for about 1 hr. The latter temperature is sufficient to reduce oxygen present on the surfaces of the metal particles but will not reduce the TiO₂. The thus-produced granulated powder contained spherically shaped particles with sizes ranging from about 15 to about 150 μm . The residual carbon in the final granulated powder was extremely low, i.e., 115 ppm.

[0066] In summary, notable advantages provided by the process methodology according to the present disclosure vis-à-vis conventional dry powder processes include:

- (1) significantly better mixing uniformity than possible with dry mixing techniques;
- (2) absence of micro and/or micro segregations;
- (3) reduced processing cost;
- (4) extremely low amount of residual carbon in ultimate granulated metal powder products; and
- (5) mixing at particle level achievable within a wide range of particle sizes of the constituent powders.

[0067] In the previous description, numerous specific details are set forth, such as specific materials, structures, reactants, processes, etc., in order to provide a better understanding of the present disclosure. However, the present disclosure can be practiced without resorting to the details specifically set forth. In other instances, well-known processing materials and techniques have not been described in detail in order not to unnecessarily obscure the present disclosure.

[0068] Only the preferred embodiments of the present disclosure and but a few examples of its versatility are shown and described in the present disclosure. It is to be understood that the present disclosure is capable of use in various other combinations and environments and is susceptible of changes and/or modifications within the scope of the disclosed concept as expressed herein.

What is Claimed Is:

1. A method of making a homogeneous granulated metal-based powder, comprising steps of:

(a) providing a preselected amount of at least one metal element or metal alloy and a preselected amount of at least one ceramic compound and/or at least one non-metallic element;

(b) forming a homogeneous slurry/suspension or wet mixture comprising said preselected amounts of said at least one metal element or metal alloy and said at least one ceramic compound and/or said at least one non-metallic element, and a liquid phase comprising at least one liquid, at least one binder material, and at least one optional additive;

(c) drying said slurry/suspension or said mixture to remove at least a portion of said liquid phase and form a powder mixture comprising partially or completely dried granules; and

(d) subjecting said partially or completely dried granules to a thermal de-binder process for effecting:

(i) additional removal of any liquid phase, if required;

(ii) removal of said at least one binder material;

(iii) reduction of carbon content;

(iv) reduction of oxygen on the surfaces or interior of the metal constituent(s); and optional

(v) partial sintering for strengthening the particles for withstanding subsequent processing.

2. The method according to claim 1, wherein:

step (a) comprises providing a preselected amount of a powder containing said at least one metal element or metal alloy, a preselected amount of another powder containing said at least one ceramic compound, and/or a preselected amount of another powder containing the at least one non-metallic element.

3. The method according to claim 2, wherein:

step (a) comprises providing preselected amounts of a plurality of powders containing respective metal elements and/or metal alloys, respective ceramic compounds, and/or respective non-metallic elements.

4. The method according to claim 3, wherein:

step (a) comprises providing preselected amounts of two powders respectively containing first and second metal elements and/or alloys and/or preselected amounts of two powders respectively containing first and second ceramic compounds and/or non-metallic elements.

5. The method according to claim 1, wherein:

step (a) comprises providing a preselected amount of a compound of said at least one metal or metal alloy and a preselected amount of a sol-gel of said at least one ceramic compound or said at least one non-metallic element.

6. The method according to claim 1, wherein:

step (a) comprises providing a preselected amount of at least one metal element or metal alloy comprising metals selected from the group consisting of: Co, Cr, Fe, Pt, Pd, Ru, Re, Ta, Al, Sm, and Nd, a preselected amount of at least one non-metallic compound selected from the group consisting of: TiO_2 , SiO_2 , MgO , Ta_2O_5 , Nb_2O_5 , Al_2O_3 , TaC , BN , ZrO_2 , HfO_2 , ZnO , CaO , La_2O_3 , WO_3 , CoO , Co_2O_3 , Y_2O_3 , Cr_2O_3 , MnO_2 , NiO , CuO , CeO_2 , Eu_2O_3 , V_2O_5 , Sm_2O_3 , Sb_2O_5 , BeO , BaO , B_2O_3 , IrO_2 , PbO , MoO_3 , ReO_2 , RuO_2 , Ag_2O , SrO , TaC , NbC , BN , B , and C .

7. The method according to claim 6, wherein:

step (a) comprises providing preselected amounts of a plurality of metal elements and/or metal alloys, ceramic compounds, and/or non-metallic elements selected from said groups.

8. The method according to any one of the preceding claims, wherein:
step (b) comprises forming said homogeneous slurry/suspension or wet mixture to comprise a liquid phase comprising at least one of water, an alcohol, and at least one organic solvent, and further comprising at least one inorganic or organic binder material.

9. The method according to claim 8, wherein:
step (b) comprises forming said homogeneous slurry/suspension or wet mixture to comprise a liquid phase comprising at least one of water, an alcohol, and at least one organic solvent selected from the group consisting of: acetone, toluene, hexane, heptane, xylene, and decane.

10. The method according to claim 8, wherein:
step (b) comprises forming said homogeneous slurry/suspension or wet mixture to further comprise at least one organic binder material selected from the group consisting of: polyvinyl alcohol (PVA), polyethylene glycol (PEG), gum arabic, other natural gums, methyl cellulose, acrylic resin emulsions, ethylene oxide polymers, water soluble phenolics, alginates, natural or synthetic waxes, flour, starches, or at least one inorganic binder material selected from the group consisting of: carbonates, nitrides, oxylates, and oxychlorides.

11. The method according to claim 8, wherein:
step (b) comprises forming said homogeneous slurry/suspension or wet mixture to further comprise at least one of a deflocculating agent, wetting agent, de-foaming agent, plasticizer, and suspending agent.

12. The method according to any one of the preceding claims, wherein:
step (c) comprises spray drying.

13. The method according to any one of the preceding claims, wherein:
step (d) comprises performing said thermal de-binder process to reduce said carbon content of said granules to less than about 500 ppm.
14. The method according to claim 13, wherein:
step (d) comprises performing said thermal de-binder process in an atmosphere comprising at least one reducing gas.
15. The method according to claim 14, wherein:
step (d) comprises performing said thermal de-binder process in an atmosphere comprising at least one reducing gas selected from the group consisting of: H_2 , NH_3 , CO, forming gas, dissociated NH_3 , H_2/N_2 mixtures, and reformed hydrocarbon gases.
16. The method according to claim 14, wherein:
step (d) comprises performing said thermal de-binder process in an atmosphere further comprising at least one weak oxidizing agent.
17. The method according to claim 16, wherein:
step (d) comprises performing said thermal de-binder process in an atmosphere comprising at least one weak oxidizing agent selected from the group consisting of: H_2O , CO_2 , air, O_2 , and air or O_2 diluted in an inert gas or a weakly oxidizing or non-oxidizing gas.
18. The method according to claim 14, wherein:
step (d) comprises performing said thermal de-binder process in an atmosphere comprising said at least one reducing gas only in a latter portion of said thermal de-binder process, and at a same or different temperature than in an earlier portion of said process.

19. A homogeneous granulated metal based or metal-ceramic based powder formed by the method according to any one of the preceding claims.

20. A homogeneous granulated metal-based powder as in claim 19, comprising at least one metal element or metal alloy comprising elements selected from the group consisting of: Co, Cr, Fe, Pt, Pd, Ru, Re, Ta, Al, and Sm, and at least one ceramic compound or non-metallic element selected from the group consisting of: TiO_2 , SiO_2 , MgO , Ta_2O_5 , Nb_2O_5 , Al_2O_3 , TaC , BN , ZrO_2 , HfO_2 , ZnO , CaO , La_2O_3 , WO_3 , CoO , Co_2O_3 , Y_2O_3 , Cr_2O_3 , MnO_2 , NiO , CuO , CeO_2 , Eu_2O_3 , V_2O_5 , Sm_2O_3 , Sb_2O_5 , BeO , BaO , B_2O_3 , IrO_2 , PbO , MoO_3 , ReO_2 , RuO_2 , Ag_2O , SrO , TaC , NbC , BN , B , and C .

21. A magnetic sputtering target fabricated from a homogeneous granulated metal-based magnetic powder of claim 20.

22. The method according to any one of claims 1 to 18, wherein:

step (a) comprises providing only a fraction of the requisite metal or metal alloy powders and a fraction or all of the requisite ceramic, oxide, and/or non-metallic element powders; and the method further comprises a step of:

(e) blending the resultant granulated powder with the balance of requisite metal or metal alloy powders and ceramic, oxide, and/or non-metallic element powders for consolidation therewith.