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(54) **SYNTHESIS OF BULK, FULLY DENSE NANOSTRUCTURED METALS AND METAL MATRIX COMPOSITES**

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(57) **ABSTRACT**

Bulk nanostructured alloys, such as aluminum 5083 alloys reinforced with 10 wt. % particulate B_4C, was synthesized by cryomilling and spark plasma sintering. Material for the alloy are selected and the selected raw materials are cryomilled, mechanical milling at cryogenic temperatures, to fabricate nanostructured alloys at low temperatures. The cryomilled powders are then degassed, and consolidated using spark plasma sintering into dense bulk materials. The material thus obtained achieved near full density bulk materials, while retaining the nanocrystalline nature. The densities of the compacts were measured using Archimedes method. XRD, SEM, TEM, and hardness testing were used to characterize the cryomilled powders and consolidated compacts.

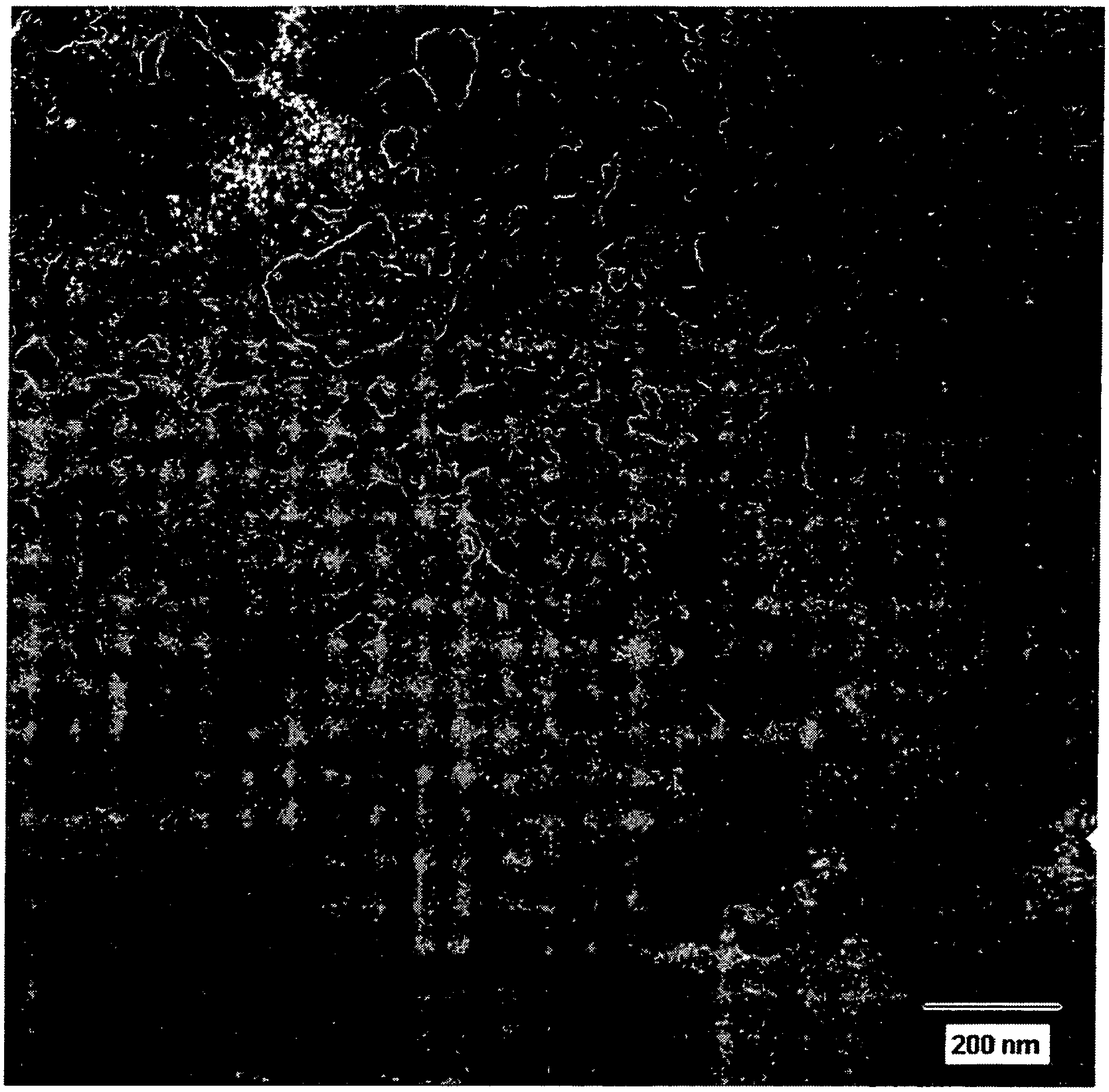

Figure 1

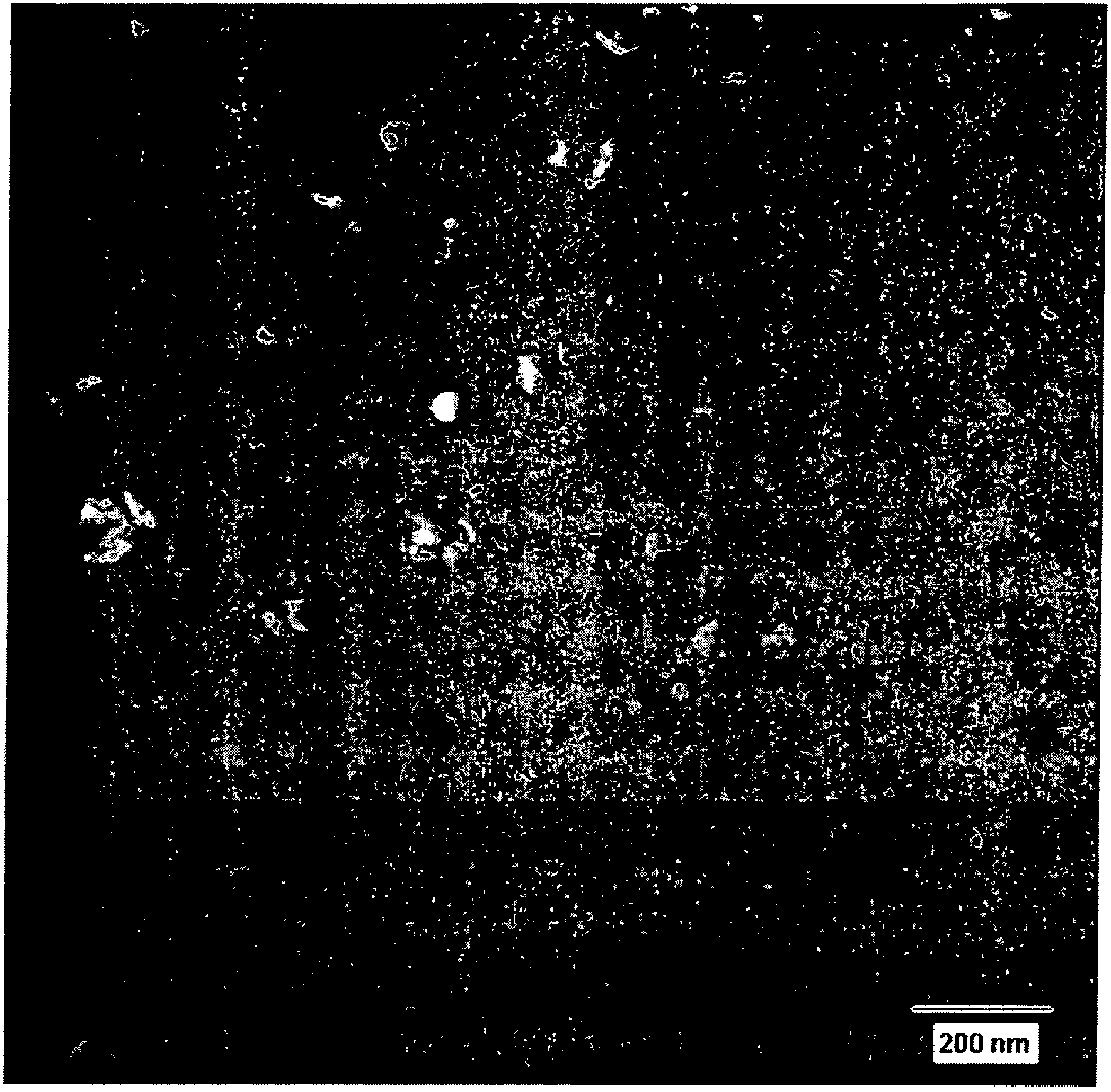

Figure 2

SYNTHESIS OF BULK, FULLY DENSE NANOSTRUCTURED METALS AND METAL MATRIX COMPOSITES

GOVERNMENT INTEREST

[0001] This invention was made with support of government grants N00014-03-C-0164 from the Office of Naval Research. Therefore, the United States government may have certain rights in the invention.

FIELD OF INVENTION

[0002] The present invention relates to the production of nanostructured materials through cryomilling and spark plasma sintering.

BACKGROUND

[0003] Nanostructured material is material with a microstructure the characteristic length of which is on the order of a few (typically 1-500) nanometers. Microstructure refers to the chemical composition, the arrangement of the atoms (the atomic structure), and the size of a solid in one, two, or three dimensions. Nanostructured materials have received increasing attention due to their superior physical and mechanical properties. They are used in the electronic industry, telecommunication, electrical, magnetic, structural, optical, catalytic, biomedical, drug delivery, and in consumer goods.

[0004] Nanostructured materials have generally been produced by (1) powder metallurgy, (2) deposition to bulk nanostructured materials, and (3) structural refinement by severe plastic deformation. In powder metallurgy processes, nanostructured materials are commonly made via mechanical milling of powder and subsequent consolidation of the powder into bulk materials. There are several disadvantages with this approach. Contamination is unavoidable during mechanical milling, either from the processing media or atmosphere, and grain growth during consolidation can occur. Modification of these methods, however, can lead to the development of processes that are more practical. For instance, it has been reported that mechanical milling under liquid nitrogen can prevent the powders from being severely oxidized from air, and small nitride or oxy-nitride particles, which are within the size of 2-10 nm, are produced in-situ during milling. These dispersoids, as they are called, can both strengthen the metal and enhance the thermal stability (i.e., control the grain growth) of the nanostructured materials. As another example, if the temperature and/or period to consolidate nanostructured powders into fully dense bulk materials can be reduced, severe grain growth can be suspended and thus the nanostructure can again be retained.

[0005] With chemical processes, nanostructured materials are created from a reaction with organometallics that precipitate particles of varying sizes and shapes. The process can, however, introduce excess carbon and/or nitrogen into the final composition. An alternative approach is the solution-gelation (sol-gel) process where ceramic production is similar to organometallic processes, except sol-gel materials may be either organic or inorganic. Both approaches involve a high cost of raw materials and capital equipment, limiting their commercial acceptance.

[0006] Physical or thermal processing involves the formation and collection of nanoparticles through the rapid cooling of a supersaturated vapor (gas phase condensation, U.S. Pat. No. 5,128,081). Thermal processes create the supersaturated vapor in a variety of ways, including laser ablation, plasma torch synthesis, combustion flame, exploding wires, spark erosion, electron beam evaporation, sputtering (ion collision). In laser ablation, for example, a high-energy pulsed laser is focused on a target containing the material to be processed. The high temperature of the resulting plasma (greater than 10,000° K) vaporizes the material quickly allowing the process to operate at room temperature. The process is capable of producing a variety of nanostructured materials on the laboratory scale, but it has the disadvantage of being extremely expensive due to the inherent energy inefficiency of lasers, and, therefore, is not suitable for industrial scale production.

[0007] Mechanical milling has been widely used to fabricate nanostructured metal powder and powder for metal matrix composites. However, it can be difficult to obtain nanostructured aluminum alloys with conventional mechanical milling, because of the high recrystallization rate due to the low melting temperature of aluminum. Cryogenic milling or cryomilling is a modified mechanical milling technique where the mechanical milling is carried out at cryogenic temperatures, usually in liquid nitrogen or a similar chilled atmosphere. Cryomilling has been employed to successfully fabricate nanostructured aluminum alloy powders and powders for aluminum metal matrix composites, which exhibit good thermal stability, because the cryogenic temperature retards the recovery of the aluminum. Strain is accumulated during cryomilling, leading to dislocation activity, ultimately causing the formation of nanoscaled grains within the cryomilled powder. The combined effect of the ultra-fine dispersion of particles formed during cryomilling and the reduced grain size is a powder that can be used to make a bulk material with relatively high strength. This type of material will also exhibit better creep resistance compared to its conventional counterpart. It has been reported that cryomilled aluminum alloys and aluminum metal matrix composite powders have nanoscaled structures with very good thermal stability. Also, cryomilling can be easily scaled up to produce tonnage quantities. Thus, cryomilling is one of the few processing approaches available for the fabrication of large quantities of nanostructured metal powders.

[0008] U.S. Pat. No. 4,818,481 to Luton et al. discloses the use of cryomilling to disperse a second phase within an aluminum alloy where the repeated fracture and cold-welding of metal powder involved in ball milling causes strain energy to be stored within the milled particles. This strain energy is introduced through the formation of dislocations, which result in decreased grain size compared to that of the starting powders. The decreased grain size also corresponds to a dispersed secondary phase within the alloy which, in turn, results in improved mechanical properties in the finished product. Different types of oxide dispersions can be dispersed within aluminum alloys by this method.

[0009] The nanostructured powders described above must be consolidated into bulk materials. Traditional consolidation approaches, such as hot pressing (HP), hot isostatic pressing (HIP), and cold isostatic pressing (CIP) have been employed for consolidation into bulk materials. U.S. Patent Application Publication No. 2004/0065173 to Fritzemeier et al. discloses aluminum alloys produced by blending aluminum with two other metals by cryomilling. The cryomilled alloy is subsequently consolidated by HIP. These consolidation methods require degassing to remove the process control agents that are normally added during cryomilling and other gases to improve the efficiency of consolidation. Further, these traditional consolidation approaches need very high pressures, on the order of GPa, which is provided by high-pressure argon, and long cycle time that can last for several hours. Aluminum particles are covered with aluminum oxide films and these oxides cannot be easily broken during consolidation which will result in less dense materials thereby negatively affecting the properties of the nanostructured materials. Therefore, a secondary processing technique, such as extrusion, is required to improve the density further and break the oxides. However, the high temperatures and long consolidation times required by these processes result in the grain growth of the nanostructured aluminum.

[0010] Therefore, there is a need for processes for making nanostructured materials where the processes are scalable for commercial production of nanostructured materials.

SUMMARY

[0011] The present invention provides methods for the synthesis of fully dense nanostructured materials, such as nanostructured aluminum alloys and aluminum metal matrix composites. The compositions thus synthesized find use in the defense industry, aerospace industry, electronics industry, and in biotechnology and drug delivery, among others.

[0012] In one aspect, the invention provides methods for the synthesis of nanostructured materials where the starting materials are cryogenically milled and consolidated by spark plasma sintering.

[0013] In another aspect, the invention provides nanostructured aluminum alloys and aluminum metal matrix composites with improved mechanical properties, such as microhardness or strength. The nanostructured aluminum alloys and aluminum metal matrix composites thus produced find use in the defense industry, aerospace industry, electronics industry, and in biotechnology and drug delivery, among others.

[0014] In another aspect, the invention provides methods for producing nanostructured materials, where the methods comprise (a) providing metal powder and optionally a reinforcement, (b) mechanically milling (a) at cryogenic temperatures to provide nanostructured powders, (c) removing gaseous components from the cryomilled powders, and (d) consolidating the cryomilled powder by spark plasma sintering. The metal powder can be Al, Be, Ca, Sr, Ba, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, W, or combinations thereof, and preferably is an aluminum alloy. The reinforcement can be oxides, carbides, nitrides, borides, metals, intermetallics, or alloys. Thus, the reinforcement can be boron carbide, silicon carbide, aluminum nitride, or aluminum oxide.

[0015] In another aspect, the invention provides methods for producing nanostructured aluminum alloys, the methods comprising (a) providing aluminum alloy and a reinforcement, (b) mechanically milling (a) at a temperature of about −150° C. to about −300° C., (c) removing gaseous components from (b), and (d) consolidating (c) by spark plasma sintering. The aluminum alloy can additionally contain a metal powder such as Fe, Co, Ni, Cu, Zn, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, W, or combinations thereof. The reinforcement can be oxides, carbides, nitrides, borides, metals, intermetallics, or alloys. Thus, the reinforcement can be boron carbide, silicon carbide, aluminum nitride, or aluminum oxide.

[0016] These and other aspects of the present invention will become evident upon reference to the following detailed description. In addition, various references are set forth herein which describe in more detail certain procedures or compositions, and are therefore incorporated by reference in their entirety.

BRIEF DESCRIPTION OF DRAWINGS

[0017] **FIG. 1** illustrates a bright field transmission electron microscopy (TEM) image for the bulk 5083 Al processes by cryomilling and SPS.

[0018] **FIG. 2** illustrates a dark field TEM image for the bulk 5083 Al processes by cryomilling and SPS.

DETAILED DESCRIPTION

I. Definitions

[0019] Unless otherwise stated, the following terms used in this application, including the specification and claims, have the definitions given below. It must be noted that, as used in the specification and the appended claims, the singular forms “a,”“an” and “the” include plural referents unless the context clearly dictates otherwise. The practice of the present invention will employ, unless otherwise indicated, conventional methods of material science and physical chemistry, within the skill of the art. Such techniques are explained fully in the literature. See, e.g., Lü L, Lai M O. Mechanical Alloying, Kluwer Academic Publishers, 1998, Boston, Mass.; Suryanarayana C. Progr Mater Sci 2001; 46: 1-184; Xie G Q, Ohashi O, Yoshioka T, Song M H, Mitsuishi K, Yasuda H, Furuya K, Noda T MATERIALS TRANSACTIONS, 42 (9): 1846-1849 SEP 2001; and Cabanas-Moreno J G, Calderon H A, Umemoto M, ADVANCED STRUCTURAL MATERIALS SCIENCE FORUM, 442: 133-142 2003.

[0020] All publications, patents and patent applications cited herein, whether supra or infra, are hereby incorporated by reference in their entirety.

[0021] The term “nanostructured material” generally refers to a material having average grain sizes on the order of nanometers. For purposes of the disclosure, nanostructured materials may include those alloys having an average grain size of 500 nanometers (nm) or less.

[0022] As used herein, “cryomilling” describes the fine milling of metallic constituents at extremely low temperatures. Cryomilling takes place within a ball mill such as an attritor with metallic or ceramic balls. During milling, the mill temperature is lowered by using liquid nitrogen, liquid argon, liquid helium, liquid neon, liquid krypton or liquid xenon. In an attritor, energy is supplied in the form of motion to the balls within the attritor, which impinge portions of the metal alloy powder within the attritor, causing repeated fracturing and welding of the metal.

[0023] As used herein, the term "powder" or "particle" are used interchangeably and encompass oxides, carbides, nitrides, borides, chalcogenides, halides, metals, intermetallics, ceramics, polymers, alloys, and combinations thereof. The term includes single metal, multi-metal, and complex compositions. Further, the terms include one-dimensional materials (fibers, tubes), two-dimensional materials (platelets, films, laminates, planar), and three-dimensional materials (spheres, cones, ovals, cylindrical, cubes, monoclinic, parallelepipeds, dumbbells, hexagonal, truncated dodecahedron, irregular shaped structures, and the like).

[0024] As used herein, the terms "nanopowders" or "nanostructured powders," are used interchangeably and refer to powders having a mean grain size less than about 500 nm, preferably less than about 250 nm, or more preferably less than about 100 nm.

[0025] As used herein, the term "alloy" describes a solid comprising two or more elements, such as aluminum and a second metal selected from magnesium, lithium, silicon, titanium, and zirconium. In addition, the alloy may contain metals such as Be, Ca, Sr, Ba, Ra, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, W, or combinations thereof.

II. Modes of Carrying Out the Invention

[0026] The present invention discloses methods for synthesizing nanostructured materials, and compositions thereof. The synthesis employs a combined processing route where cryomilling and spark plasma sintering (SPS) are used to synthesize and consolidate nanostructured materials. The methods of the invention have the advantage of having shorter consolidation time and lower consolidation temperature. The inventive methods do not require the use of high pressure gases, such as high pressure argon that is normally required by the existing methods, e.g. HIP. The inventive methods allow for suspending severe grain growth and maintaining the nanostructure due to the lower consolidation temperature and shorter consolidation time. The inventive methods do not require secondary consolidation steps, e.g. extrusion, because the potential for formation of an oxide film is lowered as a result of the process conditions: the sintering occurs in vacuum in the presence of a strong reducing agent, e.g., the graphite that is used as the film and die. Further, the consolidation of the nanostructured material to full density does not require a degassing step, and the consolidated materials have good thermal stability, i.e., grains remain in the nanometer scale even after consolidation and use. The SPS sample contains two distinct regions with different grain sizes. The small (nano) sized grains contribute to high strength, while the large (submicron) sized grains enhance the ductility of the materials. In addition, the lower processing cost of SPS compensates for the higher processing cost of cryomilling, thus making the combined processing route economically feasible and scalable.

[0027] The methods of the present invention can be used with metals with low melting temperatures, such as Ni, Fe, Cu, and Al, and mixtures thereof, or with refractory metals, such as Ti, Nb, Mo, Ta, and W, metal matrix composites, and intermetallics. In one aspect, the metal powder to be processed is pre-alloyed powder that can be used directly in the cryomilling process. In another aspect, the powder to be processed is non-alloyed powder wherein two or more different metal powders are added to the cryomill, and the cryomilling process is used to mix together the metal constituents thereby alloying the metals.

[0028] The methods of the present invention can be used with low melting metals, such as Ni, Fe, Cu, and Al, and mixtures thereof, and one or more other metals. Preferably, the starting metals are manipulated in a substantially oxygen free atmosphere. For example, if the metal is aluminum, the aluminum is preferably supplied by atomizing the aluminum from an aluminum source and collecting and storing the atomized aluminum in a container under an argon or nitrogen atmosphere. The inert atmosphere prevents the surface of the aluminum particles from excessive oxidation and prevents contaminants such as moisture from reacting with the raw metal powder. Preferably, other metals that can readily oxidize are treated in the same manner as aluminum prior to and after milling.

[0029] The metal for use in the invention can be selected from a Group 2A metal, such as Be or Mg, and mixtures thereof, a Group 3A metal, such as Al, and mixtures thereof, a Group 4A metal, such Sn or Pb, and mixtures thereof, a Group V metal, such as V or Nb, and mixtures thereof, a Group VI metal including Cr, W, or Mo, and mixtures thereof, VII metal, such as, Mn, or Re, a Group VIII metal including Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, and mixtures thereof, the lanthanides, such as Ce, Eu, Er, or Yb and mixtures thereof, or transition metals such as Cu, Ag, Au, Zn, Cd, Sc, Y, or La and mixtures thereof. Specific examples of mixtures of metals, such as bimetallics, which may be employed by the present invention include Fe—Al, Al—Mg, Co—Cr, Co—W, Co—Mo, Ni—Cr, Ni—W, Ni—Mo, Ru—Cr, Ru—W, Ru—Mo, Rh—Cr, Rh—W, Rh—Mo, Pd—Cr, Pd—W, Pd—Mo, Ir—Cr, Ir—W, Pt—W, and Pt—Mo. Preferably, the metal is aluminum, iron, cobalt, nickel, titanium, copper, molybdenum, or a mixture thereof. The metal or mixture of metals can be processed to obtain the desired grain size and grain size distribution. Examples of elemental compositions include, but are not limited to, (a) precious metals such as platinum, palladium, gold, silver, rhodium, ruthenium and their alloys; (b) base and rare earth metals such as iron, nickel, manganese, cobalt, aluminum, copper, zinc, titanium, samarium, cerium, europium, erbium, and neodymium; (c) semi-metals such as boron, silicon, tin, indium, selenium, tellurium, and bismuth; (d) non-metals such as carbon, phosphorus, and halogens; and (e) alloys such as steel, shape memory alloys, aluminum alloys, manganese alloys, and superplastic alloys.

[0030] The starting metal powder can additionally be mixed with a certain amount of reinforcement, also called ceramic composition (oxide, carbide, nitride, boride, chalcogenide), or an intermetallic composition (aluminide, silicide) or an elemental composition. Examples of ceramic composition include, but are not limited to (a) simple oxides such as aluminum oxide, silicon oxide, zirconium oxide, cerium oxide, yttrium oxide, bismuth oxide, titanium oxide, iron oxide, nickel oxide, zinc oxide, molybdenum oxide, manganese oxide, magnesium oxide, calcium oxide, and tin oxide; (b) multi-metal oxides such as aluminum silicon oxide, copper zinc oxide, nickel iron oxide, magnesium aluminum oxide, calcium aluminum oxide, calcium aluminum silicon oxide, indium tin oxide, yttrium zirconium oxide, calcium cerium oxide, scandium yttrium zirconium oxide, barium titanium oxide, barium iron oxide and silver copper zinc oxide; (c) carbides such as silicon carbide, boron carbide, iron carbide, titanium carbide, zirconium carbide, hafnium carbide, molybdenum carbide, and vanadium carbide; (d) nitrides such as silicon nitride, boron nitride, iron nitride, titanium nitride, zirconium nitride, hafnium nitride, molybdenum nitride, and vanadium nitride; (e) borides such as silicon boride, iron boride, titanium diboride, zirconium boride, hafnium boride, molybdenum boride, and vanadium boride; and (f) complex ceramics such as titanium carbonitride, titanium silicon carbide, zirconium carbonitride, zirconium carboxide, titanium oxynitride, molybdenum oxynitride, and molybdenum carbonitride.

[0031] In another aspect, the starting metal powders can be mixed with some compounds other than ceramics. Such compounds may include, for instance, organometallic compounds such as metal alkoxides, as well as nitrates, carbonates, sulfates, and hydroxides. These may be in the form of a powder or a liquid.

[0032] In the case of preparing a mixture containing ceramic and metals or alloys in obtaining the sintered compact according to the present invention, there is no particular limitation on the molar equivalents for the ceramic to be added. However, the molar ratio of metals to added ceramic reinforcement is preferably 1000:1 to about 1:1, preferably about 500:1 to about 5:1, and more preferably about 100:1 to about 10:1

[0033] Once the constituents of the metal or metal mixture and ceramic reinforcement are selected, powders can be cryomilled, wherein fracturing and welding of the metal particles is carried out in a very low temperature environment. The milling can be using shaker type mills, attritor mills, planetary mills, ball mills, or rotary mills. Preferably the cryomilling of the metal powder takes place within an attritor. The attritor is typically a cylindrical vessel filled with a large number of ceramic or metallic spherical balls. A single fixed-axis shaft is disposed within the attritor vessel, and there are several radial arms extending from the shaft. As the shaft is turned, the arms cause the spherical balls to move about the attritor. When the attritor contains metal powder and the attritor is activated, portions of the metal powder are impinged between the metal balls as they move about the attritor. The force of the metal balls repeatedly impinges the metal particles and causes the metal particles to be continually fractured and welded together.

[0034] The milling of the powders at low temperatures imparts a high degree of plastic strain within the powder particles. During cryomilling, the repeated deformation causes a buildup of dislocation substructure within the particles. After repeated deformation, the dislocations evolve into cellular networks that become high-angle grain boundaries separating the very small grains of the metal. Grain size as small as approximately 10^{-8} meter have been observed via electron microscopy and measured by x-ray diffraction. Structures having dimensions smaller than 10^{-7} meter, such as those found in the material produced at this stage in the invented process, are commonly referred to as nanostructured.

[0035] During milling, an organic polymer, such as polyethylene glycol, polyvinyl alcohol, and the like, or organic acids, such as stearic acid, ethyl acetate, ethylene bidisteramide and dodecane may be added as one of the components to be milled with the metal powder. The addition of organic components promotes the fracturing of metal particles during milling, and prevents the severe adhesion of the metal powders onto the milling media and milling tools.

[0036] During milling, the temperature of the metal powder is preferably about −150° C. or lower, such as about −300° C. Typically, the temperature of the metal powder is reduced by using liquefied inert gases, such as liquid nitrogen (bp −196° C.), liquid argon (bp −186° C.), liquid helium (bp −269° C.), liquid neon, liquid krypton or liquid xenon. The use of liquid gases is a convenient way to lower the temperature of the entire cryomilling system. Further, surrounding the metal powder in liquid gases limits exposure of the metal powder to oxygen or moisture. In operation, the liquid gas is placed inside the attritor, in contact with the metal particles and the attritor balls.

[0037] The operating parameters of the cryomill will depend upon the size of the attritor. For example, a 150 liter (40 gal) attritor is preferably operated at a speed of about 100 to 400 rpm. The amount of powder added to the attritor is dependent upon the size and number of balls within the attritor vessel. For a 150 liter attritor filled with 640 kg of 0.25" diameter steel balls, up to approximately 20 kg of metal powder may be milled at any one time. Milling is continued for a time sufficient to reach an equilibrium nanostructured grain size within the metal.

[0038] After milling, the metal alloy powder is a homogenous solid solution of aluminum and the secondary metal, optionally having other added tertiary metal components and optionally having minor amounts of metallic precipitate interspersed within the alloy and optionally having ceramic reinforcements interspersed within the alloy. Grain structure within the alloy is very stable and grain size is less than 500 nm. Depending on the alloy and extent of milling the average grain size is less than about 300 nm, and preferably may be lower than about 100 nm.

[0039] After the metal alloy powder, with the proper composition and grain structure, is produced, it is consolidated into a form that may be shaped into a useful object. The consolidation may be by hot pressing (HP), hot isostatic pressing (HIP), cold isostatic pressing (CIP), or spark plasma sintering (SPS). The consolidation is preferably by HIP or SPS, more preferably SPS. If consolidation is by HIP, the metal powder can be canned, degassed, and then compacted and welded. After consolidating, the solid mass of the metal may be worked and shaped. The consolidated metal can be extruded into a usable metal component, and forged if necessary. Further, there are no particular limitations concerning the conditions of the HIP treatment and can be varied. Further, the HIP treatment above may be carried out under an inert atmosphere such as of nitrogen, argon, or helium and the retention time at the treatment temperature and pressure may be in a range of from 0.5 to 3 hours, and particularly, approximately in a range of from 1 to 2 hours.

[0040] The metal alloy is preferably consolidated by SPS. The SPS system can be commercially obtained, such as Dr. Sinter 1050 apparatus (Sumitomo Coal Mining Co., Japan). Typically in SPS, a graphite die with an inner diameter of about 20 mm to about 100 mm is used. The larger inner diameter is selected for the fabrication of large pieces of bulk materials. The uniaxial pressure for SPS can be applied by the top and bottom graphite punches thereby eliminating the need for high-pressure argon. Typically, the alloy from cryomilling is degassed to remove the gaseous materials, including stearic acid. The removal of gaseous components is preferably carried out at a temperature between about 200° C. and 600° C., more preferably at a temperature between about 300° C. and 500° C. Then, the alloy in the SPS system is heated at a rate of about 10-500° C./min and held at the sintering temperature for about 1 min to about 60 min, preferably about 2 min to about 15 min. The sintering temperature is carried out at a temperature between about 40% and 100% of the absolute melting temperature of the metal phase, preferably between about 60% and about 95% of the absolute melting temperature of the metal phase, more preferably about 80% and about 95% of the absolute melting temperature of the metal phase. Thus, the shorter sintering time and elimination of the requirement for high-pressure argon make SPS an economically effective consolidation process.

[0041] The sintered alloy obtained by cryomilling and SPS consolidation has a relative density with respect to the theoretical density of about 99.0% or higher, preferably about 99.6% or higher, more preferably about 99.7% or higher, and particularly preferably, about 99.8% or higher. In this manner, the residual pores in the nanostructured alloy can be easily expelled resulting in complete extinction of residual pores in the sintered materials. A relative density lower than 99.0% is not preferred, because the resulting alloy exhibits impaired strength and hardness at room temperature as well as at high temperatures. Thus, the density of aluminum 5083 according to the present invention is preferably 2.63 g/cm^3, and more preferably, 2.65 g/cm^3 or higher (the upper limit is the theoretical density of the resulting material). Setting the density in the above range is preferred, because the sintered materials can be sufficiently densified for improving strength and hardness, while also improving abrasion resistance.

[0042] At all times from cryomilling through the completion of consolidation, the alloy powder is handled in an inert atmosphere, such as a dry nitrogen or an argon atmosphere or in vacuum. The inert atmosphere prevents oxidation of the surface of the alloy powder particles. The inert atmosphere further prevents the introduction of moisture to the alloy and prevents other contaminants, which might be problematic in the extruded solid, from entering the powder.

[0043] The size and distribution of grains within the nanostructured material produced by the present invention may be verified by any suitable method. One method of verification uses an X-ray diffraction pattern (XRD). XRD measurements can be performed using Cu K_α radiation in a Siemens D5000 diffractometer equipped with a graphite monochromator. The grain size of the material can be calculated on the basis of the peak broadening. The methods described above may be used to produce nanostructured materials with a certain size distribution. When one of the metals is aluminum, the sintered aluminum according to the present invention has an average grain size of 500 nm or smaller, preferably from 1 nm to about 300 nm, more preferably, from 3 nm to about 200 nm, further preferably, from 5 nm to about 150 nm. In an embodiment, the nanostructured materials comprise grains between about 3 nm and about 10 nm in size. In another embodiment, the nanostructured materials comprise grains between about 5 nm and about 50 nm in size. In still another embodiment, the nanostructured materials comprise grains between about 20 nm and about 40 nm in size. The calculation from XRD peak broadening shows us the average grain size is 25 nm for as-cryomilled Al powders, 40 nm for degassed powders, and 44-60 nm for SPS-consolidated powders depending on the sintering parameters.

[0044] Another method of verification is transmission electron microscopy (TEM). A suitable model is the Phillips CM300 FEG TEM that is commercially available from FEI Company of Hillsboro, Oreg. In order to take a TEM micrograph, the metal nanoparticles are typically thinned to achieve a foil that is thin enough for an electron beam to pass through. The TEM samples can be prepared using any of the known art procedures. For example, the powders and epoxy can be mixed to create a slurry, which can then be mounted into a stainless steel nut, sliced from a stainless steel pipe with an outside diameter of 3 mm and an inside diameter of 2 mm, to form a 3-mm diameter disk. The disk can be ground and dimpled to a thickness of approximately 30 μm using a dimpler fitted with alumina grinders. The particle size of the alumina grinders descend from a 3 μm grade to a 1 μm grade. Further thinning perforation process can be carried out using a Gatan 600 argon ion mill at the temperature of near liquid nitrogen temperature (the extension of sample holder can be soaked in liquid nitrogen) with an angle range from 22° to 10°. The TEM apparatus is then used to obtain micrographs of the particles that can be used to determine the grain size and grain size distribution of the nanostructure powder created.

[0045] The methods of the present invention synthesize sintered aluminum 5083 having high strength and hardness. More specifically, the sintered aluminum 5083 yields a Vicker's hardness of 100 or higher, preferably 120 or higher, and more preferably, 160 or higher.

[0046] The nanostructured materials of the present invention have numerous applications in industries such as, but not limited to, space shuttle and satellite components, jet aircraft components, helicopter roof control spiders and swashplates, combustion engine components, brake rotors, gear box components, missile components, armor vehicle body and components, diesel pistons, bicycle frames and components, automotive propeller shaft, corrosion sensitive applications, biomedical, sensor, electronic, telecommunications, optics, electrical, photonic, thermal, piezo, magnetic and electrochemical products.

EXAMPLES

[0047] Below are examples of specific embodiments for carrying out the present invention. The examples are offered for illustrative purposes only, and are not intended to limit the scope of the present invention in any way. Efforts have been made to ensure accuracy with respect to numbers used (e.g., amounts, temperatures, etc.), but some experimental error and deviation should, of course, be allowed for.

Example 1

[0048] Bulk nanostructured aluminum 5083 alloys reinforced with 10 wt % particulate B_4C were synthesized by cryomilling and spark plasma sintering. Coarse-grained aluminum 5083 alloy and hard B_4C, having a particle size of a few microns, were cryomilled at a temperature of −180° C. using a Szegvari attritor with the ball-to-powder ratio of 32:1 and rotation speed of 180 rpm for 8 h. A small amount of stearic acid (0.2 wt %) was added into the milling chamber as a process control agent to prevent severe adhesion of the powders onto the chamber and milling balls. The cryomilled powder was degassed at 400° C., and loaded into a graphite die and cold pressed through the punches under a load of 2000 pounds for one minute.

[0049] The powder was consolidated using spark plasma sintering apparatus under vacuum. The ramping time from room temperature to 350° C. was 3 minutes. The powders were then kept at 350° C. for 3 minutes under the uniaxial sintering pressure of 80 MPa.

[0050] The densities of the compacts thus obtained were measured using Archimedes method. The hardness at room temperature for the sintered composite was obtained by the Vicker's hardness measurement method under a load of 2.942N.

[0051] The density of the bulk materials is 2.64 g/cm^3, 99.9% of the theoretical density. The hardness for this bulk composite is 288.7 HV and the average grain size in the aluminum 5083 matrix is 56 nm.

[0052] The x-ray diffraction (XRD) pattern of sintered B_4C reinforced aluminum composites shows that the compacts are nanostructured materials.

Example 2

[0053] Bulk nanostructured aluminum 5083 alloys reinforced with 10 wt % particulate B_4C were synthesized by cryomilling and spark plasma sintering following the procedure of Example 1, except the cryomilled powder was not degassed at 400° C. before being subjected to spark plasma sintering and the powders were held at 350° C. for 2 minutes after the temperature reached 350° C. during plasma sintering.

[0054] The densities of the compacts thus obtained were measured using Archimedes method. The densities of the bulk materials were 2.65 g/cm^3, 100% of the theoretical density. XRD, and hardness testing were used to characterize the consolidated compacts, and results showed that the hardness for this bulk composite is 233.3 HV with an average grain size of 44.8 nm in the matrix.

Example 3

[0055] Bulk nanostructured aluminum 5083 alloys were synthesized by cryomilling and spark plasma sintering following the procedure of Example 2. The microstructures of the compacts thus obtained were investigated using transmission electron microscopy (TEM), shown in **FIGS. 1 and 2**. The SPS sample contains two distinct regions with different grain sizes. The region with the large grains is in the upper left corner in **FIG. 1**, and the region with the small grains is in the remainder. In this small-grained region, most of the Al grains are below 50 nm in size, and some Al grains are as small as 20 nm. As a basis for comparison, the average grain size for as-cryomilled 5083 Al powder is 25 nm, with a grain size distribution of 15-60 nm. Thus, the grain size for SPS 5083 Al in the small-grained region is comparable to the Al grains in the as-cryomilled 5083 Al powders, indicating that the small grain size can be retained after consolidation by SPS. Some grains in the cryomilled powders grew during SPS, forming the region containing the larger grains. These larger grains have a wide distribution in size, from 50 to 200 nm. The presence of the small grains in the SPS 5083 Al contributes to the higher strength of the material, while the presence of the large grains contributes to the ductility of the material.

[0056] The densities of the compacts thus obtained were measured using Archimedes method. The densities of the bulk materials were 2.63 g/cm^3, 99.0% of the theoretical density. XRD, and hardness testing were used to characterize the consolidated compacts, and results showed that the hardness for this bulk material is 165.3 HV with an average grain size of 56.6 nm.

[0057] While the invention has been particularly shown and described with reference to a preferred embodiment and various alternate embodiments, it will be understood by persons skilled in the relevant art that various changes in form and details can be made therein without departing from the spirit and scope of the invention. All printed patents and publications referred to in this application are hereby incorporated herein in their entirety by this reference.

1. A method for producing nanostructured materials, the method comprising:

(a) providing a metal powder and optionally a reinforcement;

(b) mechanically milling (a) at a cryogenic temperature (cryomilling) to provide a nanostructured powder;

(c) removing gaseous components from the cryomilled powder; and

(d) consolidating the cryomilled powder by spark plasma sintering, wherein the nanostructured material thus produced has a relative density of about 99.0% or higher and an average grain size of less than 100 nm.

2. The method of claim 1, wherein the reinforcement is selected from the group consisting of oxides, carbides, nitrides, borides, metals, intermetallics, and alloys.

3. The method of claim 1, wherein the metal powder is selected from the group consisting of Al, Be, Ca, Sr, Ba, Ra, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, and W, and combinations thereof.

4. The method of claim 1, wherein the metal powder is an aluminum alloy.

5. The method of claim 1, wherein the reinforcement is boron carbide.

6. The method of claim 1, wherein the reinforcement is silicon carbide.

7. The method of claim 1, wherein the reinforcement is aluminum nitride.

8. The method of claim 1, wherein the reinforcement is aluminum oxide.

9. The method of claim 1, wherein the reinforcement is in the form of a particulate.

10. The method of claim 1, wherein the reinforcement is in the form of a platelet.

11. The method of claim 1, wherein the reinforcement is in the form of a whisker.

12. The method of claim 1, wherein cryomilling is continued until an equilibrium grain size of the metal is reached.

13. The method of claim 12, wherein cryomilling is continued between 6 and 10 hours.

14. The method of claim 1, wherein the removal of gaseous component occurs at a temperature between about 200° C. and 600° C.

15. The method of claim 14, wherein the removal of gaseous components occurs at a temperature between about 300° C. and 500° C.

16. The method of claim 1, wherein the spark plasma sintering is carried out at a temperature between 40% and 100% of the absolute melting temperature of the metal phase.

17. The method of claim 1, wherein spark plasma sintering is carried out with different ramping rates and various holding time.

18. The method of claim 1, wherein removal of gaseous components and consolidation of the cryomilled-powder occur simultaneously, to form a fully dense material without a separate degassing step.

19. The method of claim 1, wherein the cryogenic temperature is provided by liquid nitrogen or liquid argon.

20. The method of claim 1, wherein the mechanical milling is conducted in a shaker type mill, an attritor mill, a planetary mill, a ball mill, or a rotary mill.

21. A method for producing nanostructured aluminum alloy, the method comprising:

(a) providing aluminum alloy and a reinforcement

(b) mechanically milling (a) at a temperature of about −150° C. to about −300° C.;

(c) removing gaseous components from (b); and

(d) consolidating (c) by spark plasma sintering, wherein the nanostructured aluminum alloy thus produced has a density of 2.63 g/cm^3 or higher and an average grain size of less than 100 nm.

22. The method of claim 21, wherein the reinforcement is selected from the group consisting of oxides, carbides, nitrides, borides, metals, intermetallics, and alloys.

23. The method of claim 21, wherein the aluminum alloy is aluminum and another metal powder selected from the group consisting of Be, Ca, Sr, Ba, Ra, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, and W, and combinations thereof.

24. The method of claim 21, wherein the reinforcement is boron carbide.

25. The method of claim 21, wherein the reinforcement is silicon carbide.

26. The method of claim 21, wherein the reinforcement is aluminum nitride.

27. The method of claim 21, wherein the reinforcement is aluminum oxide.

28. The method of claim 21, wherein cryomilling is continued until equilibrium grain size of the metal is reached.

29. The method of claim 28, wherein cryomilling is continued between 6 and 10 hours.

30. The method of claim 21, wherein the removal of gaseous component occurs at a temperature between about 200° C. and 600° C.

31. The method of claim 30, wherein the removal of gaseous components occurs at a temperature between about 300° C. and 500° C.

32. The method of claim 21, wherein removal of gaseous components and consolidation of the cryomilled powder occur simultaneously, to form a fully dense material without a separate degassing step.

33. The method of claim 21, wherein the temperature is provided by liquid nitrogen or liquid argon.

34. The method of claim 21, wherein the spark plasma consolidation is carried out at about 350° C.

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