NANO-COMPOSITE ENERGETIC POWDERS PREPARED BY ARRESTED REACTIVE MILLING

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ABSTRACT

A method is disclosed for producing an energetic metastable nano-composite material as well as the energetic metastable nano-composite materials produced thereby. Under pre-selected milling conditions a mixture of powdered components are reactively milled. These components will spontaneously react at a known duration of the pre-selected milling conditions. The milling is stopped at a time at which the components have been compositionally homogenized to produce nanocomposite powder, but prior to said known duration, and thereby before the spontaneous reaction occurs. The milled powder is recovered as a highly reactive nanostructured composite for subsequent use by controllably initiating destabilization thereof.
Fig. 1

Fig. 2
Fig. 15

- 44 nm
  - Ref. [163]: 73.0% of Al volume melts at bulk $T_m$

- 80 nm
  - Ref. [163]: 88.0% of Al volume melts at bulk $T_m$

- 121 nm
  - Ref. [163]: 82.7% of Al volume melts at bulk $T_m$

DSC Signal (Heat Flow), mW/mg

Temperature, °C
Fig. 16
Fig. 17

- Growth of amorphous oxide
- Amorphous → γ-Al₂O₃ transition
- Healing of γ-Al₂O₃ film
- Growth of γ-Al₂O₃ transitions
- Growth of α-Al₂O₃

TGA (mass increase)

Temperature, K

Stage I II III IV
Fig. 19

Nanocomposite powder produced by ARM [178]

Mixed nanopowders [170]

Temperature, K

Heat Flow, mW/mg, Exo-up
Fig. 21
NANO-COMPOSITE ENERGETIC POWDERS PREPARED BY ARRESTED REACTIVE MILLING

RELATED APPLICATION


GOVERNMENT LICENSE RIGHTS

[0002] The United States government may hold license and/or other rights in this invention as a result of financial support provided by governmental agencies in the development of aspects of the invention.

FIELD OF THE INVENTION

[0003] This invention relates generally to energetically reactive compositions, and more specifically relates to the preparation of metastable nano-composite materials by arrested reactive milling.

BACKGROUND OF THE INVENTION

[0004] A very high reaction enthalpy is an advantage of composite energetic formulations employing metallic fuels and solid oxidizers. However, the rates of reaction of such formulations are limited by condensed phase transport processes and are much lower than the reaction rates of monomolecular energetic formulations, e.g., TAT, HMX, RDX, etc. Current research on composite energetics aims to reduce the length scales limiting mass transfer rates and to approach the reaction kinetics achievable for monomolecular formulations. Significant efforts have been made to produce metal fuel powders with nano-sized particles. (See e.g., Dufaux, et al., Combustion and Flame 100 (1995) 350-358; Rosen, et al., Chemical and Physical Processes in Combustion Combustion Institute, Raleigh, N.C., 1999, pp. 164-167) Faster burning rates have been demonstrated with nano-sized metal powders for several applications, however difficulties in handling such powders and their incorporation into existing formulations have also been reported (Brussseau, et al., Propellants, Explosives, Pyrotechnics 27(5) (2002) 300-306). To benefit fully from the small length scale and large specific surface of nano-sized metal particles, such particles should be intimately mixed with similarly sized oxidizer particles. Progress in this direction has been reported and nanopowders of metals and metal oxides have been mixed in organic solvents forming so-called Metastable Intermetallic Composites (MIC) (Bockman, et al., CPEA Publication 712 (38th JANNAF Combustion Subcommittee Meeting) (2002) 613-624). Sol-gel processing has also been developed to produce nanostructured matrices of oxidizer materials that can be filled with metallic nano-sized fuels (Tililoton, et al., Journal of Non-Crystalline Solids 285(1-3) (2001) 338-345).

[0005] In all of the current approaches, metal nanopowders have to be synthesized in a separate process and then mixed with the oxidizer. Handling of the highly reactive nano-sized fuel particles in close contact with oxidizer is needed and some passivation is always required. In order to reduce ignition sensitivity of metal nano-powders, protective coatings are used (Maeng et al., Journal of Metastable and Noncrystalline Materials 15-16 (2003) 491-494), which typically reduce the overall enthalpy of the fuel. Nano-sized ingredient powders also make it difficult to achieve the desired high density of the final energetic formulations. In addition, the costs of synthesis, passivation, and handling of the fuel and oxidizer nanopowders are currently prohibitively high.

[0006] Commonly used energetic materials are based on monomolecular compounds, such as TNT, RDX, HMX, Cl-20, etc. (Agrawal, Recent Trends in High Energy Materials Progress in Energy and Combustion Science 1998; 24:1-30; Pagoria, et al., Thermochimica Acta 2002; 384:187-204). The maximum heat of combustion of such materials is generally limited by the enthalpy of formation of their reaction products, CO₂ and H₂O upon complete oxidation. The monomolecular energetic materials enable an exothermic reaction to occur very rapidly, with the rate controlled primarily by the chemical kinetics processes for the molecular decomposition (Tarver, Journal of Energetic Materials 2004; 22(2): 93-107; Brill, et al., Kinetics and Mechanisms of Thermal Decomposition of Nitroaromatic Explosives Chemical Reviews (Washington, D.C., United States) 1993; 93(8):2667-92). On the other hand, the energy densities of such materials are relatively low. Higher combustion energies and thus higher energy densities can be obtained from combustion metal fuels, such as Mg, Al, B, Ti, and others. The advantages of metal fuels are clear and become more significant when volumetric reaction enthalpies are compared. The main drawback of using such fuels is associated with relatively low rates of energy release. Micron-sized metal particles ignite after a fairly long delay as compared to the ignition of monomolecular energetic compounds. Such delays are usually controlled by relatively slow heterogeneous reactions leading up to the self-sustaining combustion of the metal particles (Rozenband, et al., Combustion and Flame 1992; 88 (1): 113-8; Trunov, et al. Combustion and Flame 2005; 140(4): 310-8; Trunov, et al. Combustion Theory and Modelling 2006; 10(4):603-23; Kazakov, et al. Archivum Combustionis 1987; 7(1-2):7-17). Furthermore, the rates of combustion of metal particles are often not sufficiently high to fully utilize their energetic benefits in the applications involving explosives, propellants, and pyrotechnics. For micron-sized particles such rates are commonly limited by the gas phase oxygen transport to the burning particle surface.

[0007] Combinations of conventional, micron-sized metal powders with condensed oxidizers, such as relatively unstable metal oxides in thermite compositions or ammonium perchlorate (AP) in solid propellants, do not result in significant acceleration of the metal ignition and combustion rates compared to the metal ignition in gaseous oxidizers. The heterogeneous processes comprising the metal ignition delays are usually associated with diffusion of oxidizer and/or fuel through the protective layers of metal oxide. Such layers always form on the surface of the metal oxidizing at a low temperature (prior to its ignition) so that the concentration of oxidizer outside the metal particle has only a limited effect on the rate of the critical diffusion processes. In addition, decomposition of the oxidizer typically occurs much sooner than the metal particles ignite, so that the igniting and burning metal particles are nearly always surrounded by a vapor-phase oxidizer. The delayed ignition often causes further problems, making metal combustion less efficient. For example, an issue of critical importance for metallized solid propellants is the agglomeration of unignited aluminum particles (Price, Journal of Propulsion and Power 1995; 11(4): 717-28; Babu, et al., Journal of Propulsion and Power 2002;
18(4):814-23). Such particles, initially mixed with AP and binder, melt and agglomerate before they ignite. The resulting large size agglomerates may never ignite or they ignite after very long delays. Because of delayed ignition, such agglomerates often cannot burn during the limited time they fly through the propulsion chamber. Thus, a large portion of the aluminum additive remains unburned, reducing dramatically both the efficiency of the propulsion system and obtained specific impulse.

Similar issues also explain the very limited range of application of conventional thermites. Initiation of a metal-metoxide redox reaction is quite difficult for mixed micron-sized powders and requires extended pre-heating of a relatively large or a well heat-insulated sample. Due to the high thermal conductivity of metal-metal oxide mixture, small, poorly insulated samples lose heat very rapidly, and for such samples the initial heterogeneous reaction never becomes self-sustaining.

An idealized metal-oxidizer system similar to the monomolecular energetic compound can be described: a metastable, homogeneous metal-oxidizer solution in which the components are not chemically bonded. Thus, the reaction rate would not be limited by heterogeneous transport processes and can be dramatically accelerated. It was observed that metastable metal-gas solutions form naturally inside combusting metal particles (Drezin, Progress in Energy and Combustion Science 2000; 26(1):57-78; Drezin, Combustion Explosion and Shock Waves 2003; 39(6):92-96).

Once such compounds form, they indeed react very rapidly resulting in micro-explosions and disruptive particle combustion (Drezin, et al., Combustion Science and Technology 1993; 90:79-99; Drezin, et al., Combustion Science and Technology 1992; 87:45-58; Molodetsky, et al. Proceedings of the Combustion Institute (Twenty-Sixth Symposium (Int’l) on Combustion). The Combustion Institute, Pittsburgh, p. 1919-1927, 1997; Molodetsky, et al., Combustion and Flame 1998; 112:522-32). However, it is anticipated that a relatively strong chemical bonding occurs in such solutions which would limit their energy density and thus respective practical applications.

It appears that a practically optimized metal-based energetic material would have the reactive components mixed on a scale as fine as possible, as long as significant chemical bonding between components is prevented. This naturally leads to the idea of using materials with high specific surface area, or materials divided down to the nanoscale in order to reduce ignition delays and accelerate combustion of metals, as proposed by Danen, et al., U.S. Pat. No. 5,266,132; Nov. 30, 1993.

SUMMARY OF THE INVENTION

In a first aspect, the present invention provides nano-structured composite energetic materials provided by using arrested reactive milling of powdered mixture of metals and oxidizers for the metals, or by such milling of mixtures of starting solid components capable of highly exothermic reaction. The resulting materials are micron-sized powders that can be handled using conventional processing techniques. Each particle comprises a fully dense mixture of the reagents with a three-dimensional nanosized structure. The components may be, for instance, a fuel and oxidizer, e.g., thermitic compositions, or highly reactive combinations of metals or metals and metalloids, e.g., B—Ti, B—Zr, Al—Ni or others. A fresh metal surface may be produced during synthesis but most of it is never exposed to oxidizing environment, unlike the fresh metal surface of the nanosized metal powders. The interface between the reactants may be formed at low temperatures and therefore, passivating layers may not be produced on the fresh metal surfaces to the same degree as for blends of nanometer sized powders or layered nanocomposites produced at elevated temperatures by sputter deposition (Blaubom, et al., Journal of Applied Physics 94(5) 2003 2915-2922).

Reactive Milling has been observed to trigger spontaneous combustion-like reactions in a number of reactive systems. Such a spontaneous reaction is likely if the adiabatic reaction temperature of the components exceeds 1800 K (Takacs, Progress in Materials Science 47:355414 (2002); Munir, et al., Materials Science Report 37(7-8) (1989) 277-365). Such spontaneous reactions show very high reaction rates desirable for many applications of energetic materials. In the present invention reactive milling is adapted to prepare highly reactive composites. Such materials are obtained just before the spontaneous reaction would have occurred during milling so that the reaction can be controllably initiated later. In order to prepare such materials, the time of spontaneous initiation must be known as accurately as possible. Current theoretical treatment of the milling process is not sufficiently advanced to predict initiation reliably. Therefore, in the process of the invention a parametric experimental investigation establishes the conditions leading to the spontaneous reaction for each composition of interest. This parametric investigation may not be necessary when the theoretical treatment of the milling process is developed sufficiently to predict initiation reliably.

The nano-structured composite energetic materials of the present invention are preferably powders having composite particles and feature interfaces between the composite components that are different from the interfaces of materials previously available. The nano-structured composite energetic materials of the present invention display upon heating different heat flow traces recorded by differential scanning calorimetry (DSC) than materials with identical chemical compositions prepared by other means and available previously. In some embodiments, the nano-structured composite energetic materials of the present invention undergo an exothermic reaction more quickly or at a lower temperature than materials previously available. In some embodiments, the nano-structured composite energetic materials of the present invention undergo an exothermic reaction in a time that is about 10%, 20%, 25%, 30%, 40% or 50% or more shorter than the time required for materials previously available to undergo a similar or the same reaction at a given heating rate. In some embodiments, the nano-structured composite energetic materials of the present invention begin to react in an exothermic reaction at a temperature that is at least about 10%, 15%, 20%, 25%, 30%, 40% or 50% or more lower than the temperature at which materials previously available begin to react in the same or a similar reaction at a given heating rate. In other embodiments, the nano-structured composite energetic materials of the present invention begin to react in an exothermic reaction at a temperature that is about 25, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 225, 250, 275, 300 or more degrees Kelvin lower than the temperature at which materials previously available begin to react in the same or a similar reaction at a given heating rate. In still other embodiments, the nano-structured composite energetic materials of the present invention begin to react in an exothermic reaction with a
different number of peaks recorded by DSC and substantially different peak shape of the reaction curve recorded by DSC as compared to the materials previously available and reacting in the same or similar reaction at a given heating rate. In yet other embodiments, the nano-structured composite energetic materials of the present invention react in an exothermic reaction at a lower temperature and the reaction occurs more actively than the materials previously available prepared by other means. That is, in these embodiments, the exothermic features such as broad and individual peaks may be difficult or impossible to separate. In such embodiments, the nano-structured composite energetic materials of the present invention may react in an exothermic reaction with a broad exothermic feature starting at about 400°, 450° or 500° K and increasing up to about 800°, 850°, 900° or 950° K.

[0014] The nano-structured composite energetic materials of the present invention are preferably in powder form with composite powder particles having interfaces between the composite components that are different from the interfaces of materials previously available. As such, particle sizes and inclusions are different from materials produced by other means. In preferred embodiments, most or all of the particles are between 1-100 microns in diameter. In other embodiments, at least about half of the particles are smaller than about 50 microns in diameter, or at least about half of the particles are smaller than about 40 microns, 30 microns or 20 microns in diameter. In some embodiments, most or all of the inclusions in the material are about 10-1,000 nanometers in diameter. In other embodiments, most or all of the inclusions in the material are about 30-300 nanometers in size, or 40-250 nanometers in diameter or 50-200 nanometers in diameter. The nano-structured composite energetic materials of the present invention are denser than similar powdered materials produced by other means. They may be, for instance, at least about 10%, 15%, 20%, 25%, 30%, 40%, 50%, 60%, 70%, 80% or more denser than similar powdered materials of the same elements produced by other means. In some embodiments, they may even be two or three or more times denser than similar powdered materials of the same elements produced by other means.

[0015] In preferred embodiments, the nano-structured composite energetic materials of the present invention are powders, and they undergo more rapid ignition than similar materials of the same elements produced by other means at a given heating rate. In some embodiments, the nano-structured composite energetic materials of the present invention substantially complete an ignition reaction in at least about 5%, 10%, 15%, 20%, 25%, 30%, 40%, or even 50% or more less time than the time required for similar materials of the same elements produced by other means at a given heating rate to substantially complete an ignition reaction. In some instances, the nano-structured composite energetic materials of the present invention may substantially complete an ignition reaction in about 500, 600, 700, 800, 1000, 1200, 1400, 1500, 1600, 1800 or 2000 μsec.

[0016] In preferred embodiments, the nano-structured composite energetic materials of the present invention are powders that can be mixed with binders, such as polymers, organic solutions, or other materials, and the composite flow behavior of the resulting mixtures is substantially different than the composite flow behavior of similar mixtures using identical binders and powder additives having chemical reactivities similar to those of the nano-structured energetic materials. In some embodiments, the composite flow viscosity of the powder-binder mixtures prepared using nano-structured composite energetic materials of the present invention is substantially lower than the composite flow viscosity of mixtures prepared using identical binders and powder additives having chemical reactivities similar to those of the nano-structured energetic materials. In some embodiments, the composite flow viscosity for the powder-binder mixtures prepared using nano-structured composite energetic materials of the present invention is at least about 5%, 10%, 15%, 20%, 25%, 30%, 40%, or even 50% or more less than the composite flow viscosity of mixtures prepared using identical binders and powder additives having chemical reactivities similar to those of the nano-structured energetic materials.

[0017] In a second aspect, the present invention provides a method for producing an energetic metastable nano-composite material. Under pre-selected milling conditions a mixture of powdered components is reactively milled. These components will spontaneously react after a known time duration specific for the pre-selected milling conditions. The milling is stopped at a time at which the components have been compositionally homogenized to produce nanocomposite particles, but prior to said known duration, and thereby before the spontaneous reaction occurs. The milled powder is recovered as a highly reactive nano-structured composite for subsequent use by controlling initiatively destabilization thereof. During recovery and handling, only the external surface of the particles is exposed to oxygenated environment and passivated by oxidation. Most of the freshly produced reactive metal interfaces remain within the nanocomposite material and retain their high reactivity.

[0018] In a preferred procedure for practicing the invention the milling is effected in a ball mill, where the pre-selected conditions include the number of balls; the ball diameter and ball material; the ratio between the mass of balls and the mass of the said components; the material, size, and shape of the milling container; the temperature of the milling container, the presence or absence of milling aids such as surfactants; and the mill operating parameters used during the milling operation, which for example in a vibratory ball mill would include oscillating rate and amplitude. On the other hand, in a stirred mill such as the “Attritor,” rotational speed of the stirrer is such an operating parameter. Similarly, in a planetary mill rotational speed of the milling vial is such an operating parameter.

[0019] In some embodiments, the present invention features a method for systematically producing an energetic metastable nano-composite material by (a) reactivity milling a mixture of powdered components that spontaneously react at a known duration of said milling; (b) stopping said milling at a time at which said components are compositionally homogenized on a nanoscale to produce a nanocomposite powder, but prior to said known duration, and thereby before said spontaneous reaction occurs; and (c) recovering as a product the milled powder as a nanostructured composite for subsequent use by controllably initiating destabilization thereof. The milling may be effected in a ball mill, and the pre-selected conditions may include the number of balls, the ball diameter and ball material, the ratio between the mass of balls and the mass of the components, the material, size, and shape of the milling container, the temperature of the milling container, the presence or absence of milling the compositions, and the mill operating parameters used during the milling. In some embodiments, the reactive milling may be affected in a vibratory mill in which the containers for the
products being milled is agitated at high frequency in a complex cycle based on motion in three orthogonal directions. In some embodiments, reactive milling is depicted in a stirred mill. In some embodiments, reactive milling is depicted in a planetary mill. In some embodiments, reactive milling is depicted in a planetary mill with the milling containers cooled by an air-conditioned air flow. In some embodiments, reactive milling is depicted in an attritor mill with the milling container cooled by liquid nitrogen. Likewise, the known duration may be experimentally determined for the components subjected to milling. In some embodiments, the components comprise a metal and an oxidizer for the metal. The components may be at least a pair of reactive metals. The components may contain at least a pair of thermite reactants. In some embodiments, the reduced product may contain particles in the 1-50 µm range. In some instances, the adiabatic reaction temperature of the components exceeds 1800 K. The present invention also provides the product produced by the methods described.

In some embodiments, the methods feature a method for systematically producing an energetic movable nano-composite material by (a) selecting starting components as two or more powdered materials capable of a highly exothermic reaction; (b) reactivating the milling starting components to achieve homogeneity; (c) stopping said milling at a time at which the components are compositionally homogenized on the nanoscale to produce a nanocomposite powder, but prior to initiation of an exothermic reaction; and (d) recovering as a product the milling powder as a reactive nano-composite for subsequent use by controllably initiating destabilization thereof. In some instances, the milling is performed under pre-selected milling conditions providing transfer of energy from milling to the powered components required to produce homogeneity. Likewise, in some instances the milling is performed under pre-selected milling conditions according to $t = \text{const}/C_K$ where $t$ is milling time, $C_K$ is a charge ratio defined as a ratio of mass of milling tools to mass of the powered components and const is a constant depending upon type of milling equipment. The present invention also provides the product produced by these methods described as well.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In some embodiments, the methods feature a method for systematically producing an energetic movable nano-composite material by (a) selecting starting components as two or more powdered materials capable of a highly exothermic reaction; (b) reactivating the milling starting components to achieve homogeneity; (c) stopping said milling at a time at which the components are compositionally homogenized on the nanoscale to produce a nanocomposite powder, but prior to initiation of an exothermic reaction; and (d) recovering as a product the milling powder as a reactive nano-composite for subsequent use by controllably initiating destabilization thereof. In some instances, the milling is performed under pre-selected milling conditions providing transfer of energy from milling to the powered components required to produce homogeneity. Likewise, in some instances the milling is performed under pre-selected milling conditions according to $t = \text{const}/C_K$ where $t$ is milling time, $C_K$ is a charge ratio defined as a ratio of mass of milling tools to mass of the powered components and const is a constant depending upon type of milling equipment. The present invention also provides the product produced by these methods described as well.
FIG. 20 demonstrates ignition delays measured for laser ignition of Al—MoO₃ thermite powders prepared with aluminum particles of different sizes (158).

FIG. 21 provides results of experiments on ignition of different powders in heterogeneous shock tube experiments (196). Emission intensity at 486 nm is shown versus time for four energetic materials in 30% O₂/70% N₂. The ambient temperature is 2250 K and the ambient pressure is 3.0 atm. The inset shows a magnified temporal region soon after endwall reflection.

FIG. 22 provides isoconversion analysis of DSC and ignition data for nanocomposite powders with bulk composition 2Al+MoO₃ prepared by ARM (178).

DETAILED DESCRIPTION OF THE INVENTION

Manufacturing of Reactive Nanopowders

Nanosized Aluminum

Nanosized aluminum powder or nanoaluminum (n-Al) is the most common component of metal-based reactive nanomaterials, while other nanopowders, e.g., boron, magnesium, or zirconium have also been considered (Kuo, et al., Materials Research Society Symposium Proceedings, 800 (Synthesis, Characterization and Properties of Energetic/Reactive Nanomaterials) Materials Research Society, p. 3-14, 2003). The popularity of n-Al is understandable because it is often considered as a potential replacement for the conventional aluminum powders and flakes widely used in explosives, propellants, and pyrotechnics. In fact, the rapid acceleration of research in the area of reactive nanocomposite materials can be readily traced to the development in the n-Al manufacturing and to the time it became available for experiments more than a decade ago. The methods of manufacturing n-Al can be broadly classified into those involving vapor phase condensation and liquid phase chemistry.

One of the first methods described in the literature was production of n-Al by exploding electrically heated wires, pioneered by Russian scientists (Zelinski, et al., Fizika i Khimiya Obrabotki Materialov 1984; (1):57-9 (in Russian); Yavorovsky, Patent of Russian Federation No. 2048277, 1995; Yavorovsky, et al., Patent of Russian Federation No. 2048278, 1995; Ivanov, et al., Pyrotechnics 2003; 28(6):319-33). This method continues to be developed around the world (Jiang, et al., IEEE Transactions on Plasma Science 1998; 26(5): 1498-501; Kwon, et al., Scripta Materialia 2001; 44:2247-51; Sarathi, et al., Materials Characterization 2007; 58:148-55; Ivanov, et al., Kuo, editor, Challenges in Propellants and Combustion 100 Years after Nobel, Begell House, New York, 1997; p. 636-45; Tepper, Powder Metallurgy 2000; 43(4):320-2) and are available commercially. Aluminum nanopowders are also produced from condensing aluminum vapor generated when a thin aluminum wire is vaporized by a strong electric current passing through it. Nanoparticles of many other metals and alloys were also obtained (Tepper, Metal Powder Report 1998; 53(6):31-33; Kwon, et al., Proceedings—9th Russian-Korean International Symposium on Science and Technology, KORUS-2005 1, art. no. 1507888, 2005, p. 211-3; Wang, et al., Materials Science and Engineering 2001; A307:190-4). Characteristic transmission electron microscope (TEM) images of aluminum nanopowders obtained by explosively heated wires are shown in FIG. 9. It was proposed that the required current density should exceed 10¹⁰ A/m² (Kwon, et al., Scripta Materialia 2001; 44:2247-51). It was also proposed that the average size of the produced particles is inversely proportional to the cube of the energy released into the wire (Rossi, et al., Journal of Microelectromechanical Systems 2007 16(4): 919-31; Kwon, et al., Scripta Materialia 2001; 44:2247-51). In various investigations, the characteristic wire diameter varied from tens to hundreds of microns. Specific electric circuits designed to produce such pulses were described in many publications (Romanova, et al., Czechoslovak Journal of Physics 2006; 56(Suppl. B):B349-B356; Sedoi, et al., IEEE Transactions on Plasma Science 1999; 27(4):845-50; Chemezeva, et al., IEEE 18th Int. Symp. on Discharges and Electrical Insulation in Vacuum-Eindhoven-1998, p. 48-5132-34). A high-voltage source (5-30 kV) is commonly used to produce a current pulse on the order of several thousands of amperes. The pulse duration varies from nanoseconds (Romanova, et al., Czechoslovak Journal of Physics 2006; 56(Suppl. B):B349-B356), achieved using customized electronic components, to several microseconds (Jiang, et al., IEEE Transactions on Plasma Science 1998; 26(5):1498-501) produced using common L-C circuits. The underlying physics of the wire explosion remains the subject of current investigations but is outside the scope of this paper. For preparation of nanopowders, the wire explosion is commonly set up in an inert gas environment. The particles are collected on the walls of the explosion vessel. The sizes of the obtained particles typically vary over a fairly broad range—from 10-20 nm to microns. The effects of pressure, gas environment, electric pulse characteristics, and other experimental parameters were studied (Zelinski, et al., Fizika i Khimiya Obrabotki Materialov 1984; (1):57-9 (in Russian); Jiang, et al., IEEE Transactions on Plasma Science 1998; 26(5):1498-501; Kwon, et al., Scripta Materialia 2001; 44:2247-51; Sarathi, et al., Materials Characterization 2007; 58:148-55; Ivanov, et al., Kuo, editor, Challenges in Propellants and Combustion 100 Years after Nobel, Begell House, New York, 1997; p. 636-45). Jiang, et al., IEEE Transactions on Plasma Science 1998; 26(5):1498-501 established that a higher pressure results in the formation of coarser particles. On the other hand, it was reported that an increased pressure of the inert gas results in an increased yield of aluminum nanoparticle (Sarathi, et al., Materials Characterization 2007; 58:148-55). Aluminum nitride was formed in the experiments performed in nitrogen (Sarathi, et al., Materials Characterization 2007; 58:148-55; Kwon, et al., Applied Surface Science 2003; 211; 57-67). The modifications of this technique include automation of the wire feed into the discharge region, setting up a flowing gas system, and altering the gas environment to passivate the aluminum nanoparticles (Tepper, Powder Metallurgy 2000; 43(4):320-2; Tepper, Metal Powder Report 1998; 53(6):31-33). In particular, treatment of the nanopowders in environments with low partial pressure of oxygen (e.g., 0.01% of the total pressure) results in the formation of protective oxide coatings which effectively stop further oxidation of nanoparticles during their handling and storage. Passivation is commonly accomplished as a separate processing step, in which the chamber filled by inert gas for powder production is evacuated and refilled with an oxidizing gas mixture. Other approaches have also been considered in which the powders were passivated by fluoro polymers, stearic and oleic acids, and aluminum diboride (Kwon, et al., Applied Surface Science 2003; 211; 57-67; Gronov, et al., Powder Technology 2006; 164: 111-5). The
advantages of preparing n-Al from electro-exploded wires include the method’s relative simplicity and the efficient use of electric energy. The main disadvantages are the relatively low production rate and difficulties in obtaining the product powders with a useful narrow size distribution.

[0046] Other techniques for the production of n-Al, including evaporation of bulk aluminum samples or aerosolized micron-sized powders followed by controlled vapor condensation, have been discussed in the literature (Granqvist, et al., Journal of Appl. Phys. 1976; 47(5):2200-19; Puszyński, Proceedings of the 29th International Pyrotechnics Seminar. Publisher: Defense Science & Technology Organization, Pyrotechnics Group; 2002, p. 191-202; Schefflan, et al., Journal of Energetic Materials 2006; 24(2): 141-56; Pivkina, et al., Journal of Thermal Analysis and Calorimetry 2006; 86(3): 733-8; Munz, et al., Pure Appl. Chem. 1999; 71(10): 1889-97; Phillips, et al., U.S. Pat. No. 6,689,192 B 1 20040210, 2004: Champion Y. Annales de Chimie (Cachan, France) 2006; 31(3); 281-94; Miziolek, The AMPTLAC Newsletter 2002; 6(1):43-8 and some of them were commercialized. Commonly, condensation in a low pressure (less than 10 torr or 1.3 kPa) inert gas results in the formation of nanoparticles, while higher pressures result in increased particle sizes. Condensation of metal vapors in lighter inert gases (e.g., He vs Ar or Xe) results in respectively finer particle sizes (Granqvist, et al., Journal of Appl. Phys. 1976; 47(5): 2200-19). Most commonly, a crucible containing bulk aluminum is heated in a flowing inert gas environment. Radiative heaters, induction heaters, lasers, electric arcs, or special high temperature furnaces have been used to vaporize the bulk aluminum sample. Of particular interest are devices using arc or induction plasma to evaporate precursor material and to further use the plasma flow to transfer the superheated vapor to the quenching zone (Boulos, et al., US Patent Application 20070029291, 2007; Choi, et al., Repub Korean Kongkang Taeho Kongbo 2008). The AI vapor is carried out into a passivation section where the inert gas is mixed with a small amount of oxygen. Finally, the passivated powder is collected thermophoretically. Miziolek, The AMPTLAC Newsletter 2002; 6(1):43-8 show aluminum wire feed into a vacuum chamber and evaporated from a heated ceramic boat. The condensation occurred in a helium or argon gas stream at pressures in the range of 2-16 torr. Many processing details remain proprietary and were never published. Other examples of devices producing n-Al are described in refs. (Tepper, Powder Metallurgy 2000; 43(4):320-2) and (Granqvist, et al., Journal of Appl. Phys. 1976; 47(5):2200-19).

[0047] Particle growth from condensing vapor has been the subject of multiple theoretical studies, some of which specifically focus on Al, e.g., (Panda, et al., NanoStructured Materials 1995; 5(7/8):755-67). It was shown that nanoparticles form in a relatively narrow temperature range. Finer particles are produced at higher cooling rates. In addition, low evaporation temperature, low pressure or low metal vapor concentration are desired. Particle nucleation and growth were considered theoretically (Puszyński, et al., Proceedings of the 4th World Congress on Powder Technology, Sydney, Australia, Paper 164, 2002) and the effect of different gas environments was explored. It was suggested based on both experiments and calculations, that carrying out the synthesis in helium results in much finer size particles compared to using argon. It was further confirmed that higher pressures result in coarser particles. In another study, it was found that coalescence of colliding nanoparticles results in a substantial reduction of the surface energy and resulting temperature increase of the product particle (Lehtinen, et al., Aerosol Science 2002; 33:357-68). This temperature increase affects the final dimensions of the growing nanoparticles (Mukherjee, et al., Journal of Chemical Physics 2003; 119:3391-404). There are now numerous theoretical papers on nanoparticle condensation from vapors, covering a variety of metals and operating conditions.

[0048] An example of using modeling for the design of nanopowder producing equipment is presented by Schefflan, et al., Journal of Energetic Materials 2006; 24(2): 141-56. Particle growth by nucleation and coagulation is considered theoretically. The problem is solved numerically. Numerical solutions offer the advantage of exploring the effects of specific, system-dependent temperature profiles, gas concentrations, etc. For example, the effect of different temperature profiles on the product particle size distribution is reported in (Schefflan, et al., Journal of Energetic Materials 2006; 24(2): 141-56).

[0049] Modifications of the generic approach based on physical vapor condensation include alloying or doping aluminum with various additives. For example, preparation of n-Al with added barium is described by Pivkina, et al., Journal of Thermal Analysis and Calorimetry 2006; 86(3): 733-8. Such readily oxidizing additives reportedly increase the reactivity of the produced aluminum and enable it to rejet at lower temperatures as compared to the pure powders. Similar to the n-Al produced by wire explosion, post-processing steps are used to passivate the surface of the nanoparticles. Both treatment in low-pressure gaseous oxygen environment and processing powders in various liquid solutions (such as oleic acid and phenyltrimethoxysilane (Puszyński, et al., Materials Research Society Symposium Proceedings 2006; 896:147-58)) have been reported.

[0050] Variations of the bulk aluminum heating technique were reported in by Puszyński, et al., Materials Research Society Symposium Proceedings 2006; 896:147-58 and Park, et al., J. Physical Chemistry B. 2005; 109(15):2920-9) in which aluminum was heated in an arc discharge or ablated by a Nd:YAG laser. The nanoparticles produced were introduced into cold argon environment for laboratory measurements which did not require substantial amounts of material. In laboratory scale measurements the particle size distributions were well-controlled. However, currently, scaling up the n-Al production using such heating techniques remains impractical.

[0051] Coating of magnetic metallic particles with carbon was reported for the arcs operated in a flow of methane (Dong, et al., J. Appl. Phys. 1999; 86(12):6701-6; Zhang, et al., Journal of Physics: Condensed Matter 2001; 13(9):1921-9). In a modification of the latter approach, aluminum was used as a consumable anode of the microwave discharge operated in natural gas to produce aluminum nanoparticles coated with a thin protective layer of carbon (Ermollie et al., Nanotechnology 2002; 13:638-43). Carbon coated aluminum nanoparticles were also obtained when aluminum nanoparticles generated by arc- or laser ablation of an aluminum target were quenched in an argon-ethylene flow (Park, et al., Journal of Nanoparticle Research 2006; 8: 455-64). Single-particle mass spectrometry measurements reported in (Park, et al., Journal of Nanoparticle Research 2006; 8: 455-64) showed that carbon coatings remain stable at the temperatures exceeding 900° C. and thus are attractive for protection of
n-Al powders. Unfortunately, the reported production rates for carbon-coated n-Al powders were very low and not yet suitable for the manufacture of such powders.


[0053] Wet chemistry techniques are attractive for the commercial synthesis of aluminum nanopowder because of the inherent safety of handling the reactive powder under liquid and the ability to readily functionalize the particle surface. However, we are unaware of any aluminum nanopowders produced by wet chemistry techniques on the commercial or on a practically interesting scale. Higa et al., U.S. Pat. No. 6,179,899 nanosized aluminum powders were prepared by decomposing alane-adducts in organic solvents under an inert atmosphere. Effective adduct species were reported to include trialkyl amines, tetramethylethylene-diamine, dioxane, and other aromatic amines and ethers. Reportedly, highly uniform spheres were obtained with particle size selectable in the range of about 65-500 nm by adjusting the catalyst concentration and by varying the concentration of the adduct species. As typical for all reported wet chemistry techniques, the methodology is based on careful and slow mixing of measured amounts of the starting solutions followed by continuous stirring and drying the product. Such a methodology is not well suited for scaled up production and substantial modifications are necessary to obtain practical quantities of the desired reactive nanopowders.

[0054] Despite these limitations of the wet-chemistry approach, surface passivation remains an important safety and handling issue and current research is focused on preparing high quality and well-passivated powders (Foley, et al., Chemistry of Materials 2005; 17(16): 4086-91; Jouet, et al., Chemistry of Materials 2005; 17(11):2987-96; Jouet, et al., Materials Science and Technology 2006; 22(4):422-429). For example, surface layers of transition metals were formed on Al nanoparticles to prevent them from oxidation in surrounding air (Foley, et al., Chemistry of Materials 2005; 17(16): 4086-91; Gao, Chinese Patent CN 101041180 A 20070926, 2007). Foley, et al., Chemistry of Materials 2005; 17(16): 4086-91) report aluminum nanopowder was synthesized by thermal decomposition of an alane solution in the presence of a titanium catalyst under an inert atmosphere. Gao, Chinese Patent CN 101041180 A 20070926 report the nanopowder was formed upon mixing and drying of aluminum dissolved in NaOH co-mixed with a nickel salt solution. In both cases, aluminum nanoparticles served as a reducing agent for the transition metal complexes, so that reduced metal films were produced on the aluminum surface. In a different passivation approach, aluminum nanopowders coated with non-metallic self-assembled monolayers (SAMs) were prepared (Jouet, et al., Chemistry of Materials 2005; 17(11):2987-96; Jouet, et al., Materials Science and Technology 2006; 22(4):422-429).

Nanoscale Al particles were prepared in a solution by catalytic decomposition of the Al-methylpyrrolidinololane adduct by titanium(IV) isopropoxide; followed by in situ coating using organic SAMs (e.g., diethyl ether solutions of perfluorotetradecanoic acid, perfluororonancolic acid or perfluoroundecanoic acid). The protective layer is clearly fairly thick resulting in the overall reduction of the energy density of such materials.

[0055] A sonochemical approach was adapted to synthesize aluminum nanopowders (Harruff, et al., South-Eastern Regional ACS meeting, Greenville, S.C. October, 2007). In this technique, a solution is prepared in which acoustic cavitation is induced. The cavitation results in the formation of small regions heated to about 5000 K, which cool very rapidly, at the rates up to 10^11 K/s. Volatile compounds trapped in these regions decompose and aggregate to form particles with characteristic dimensions of about 10-60 nm. The early efforts aimed at production of reactive n-Al appear to be promising because of the potential capabilities to control the product properties and scale the production up.

[0056] New approaches to passivating the surface of n-Al continue to be developed and substantial progress is expected in this area in the near future. For example, encapsulation of aluminum nanoparticles in polystyrene was recently described by Zhang, et al., Henneng Cailian/Chinese Journal of Energetic Materials 2007; 15 (5):482-4 and was shown to be effective in preventing aluminum oxidation. An approach similar to that proposed by Wilson, et al., Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films 2008; 26(3): 430-7 resulting in the formation of atomic layer deposition of refractory metal on surface of metallic nanoparticles may also be of interest in the future.

Additional Nanopowders

[0057] Highly exothermic intermetallic, metal-metallloid, and thermite reactions are commonly exploited in metal-based reactive nanomaterials. Additionally nanoscale components include metals other than aluminum (Mg, Zr, Ti, Ni, etc.), boron (a metallloid), and metal oxides. Recently, nanosized silicon powders and nanoporous silicon wafers were considered for energetic applications (Son S. F. Personal communication, 2008). Porous silicon wafers are typically prepared by electrochemical etching of Si wafers in different electrolytes (Sun, et al., Advanced Materials 2007; 19(7): 921-4). Because of multiple applications in electronics and electro-optical devices, synthesis of Si nanoparticles was addressed by many researchers in the past. Some of the related techniques are described by El-Shall, et al., 2003 Journal of Physical Chemistry B 107 (13), pp. 2882-2886; Makimura, et al., 2002 Japanese Journal of Applied Physics, Part 2: Letters 41 (2 A), pp. 144-146 and Dang, et al., 2007 ECS Transactions 2 (7), pp. 255-265). Use of microwave plasma reactors for production of silicon nanoparticles should be mentioned in particular because of substantial practical benefits and potential for the scaled up production (Giesen, et al., Journal of Nanoparticle Research 2005, 7(1): 29-41).
Production of most metal nanopowders is accomplished using one or more of the same techniques described above for aluminum. Such powerful energy sources as lasers or arcs make it possible to vaporize practically any metal and thus enable vapor-condensation based techniques. Reduction of various metallic complexes in solution represents another common approach for generating metal nanopowders. In both cases, the cost of the nanopowders is relatively high and the production rates are limited. Commerically available boron powders have not been marketed as nanopowders, but they typically have primary particles with sizes of the order of 100 nm. The fine primary particles are strongly agglomerated while the specific surface of the material is similar to that of a spherical nanosized powder. The surface features of individual particles are very fine, but the particle shapes are irregular. In order to achieve effective mixing of such a powder with other components, advanced mixing techniques are required.

Metal oxides are often available commercially in various size ranges and thus need not be always produced specifically for preparation of reactive nanocomposite materials. At the same time, development of optimized and customized technologies for preparation of nanosized oxide powders remains an active research area. For example, detailed procedures for preparing nano-sized MoO₃ are described by Khan, et al., WO 02/38239 A1. The process is based on sublimation of a precursor material followed by the controlled condensation of MoO₃. The condensation occurs in a stream of oxygen-rich gas to enable complete oxidation of the condensing molecules. A variant of this approach is described by Mitra, et al., Thin Solid Films 2008; 516:798-802 where a thin, electrically heated metal filament is used as the source of metal vapor.

Many nano-sized oxide powders were readily produced by chemical vapor deposition-based techniques. In particular, various flame synthesis approaches (Rosner, Eng. Chem. Res. 2005; 44:6045-55; Pratsinis, Progress in Energy and Combustion Science 1998; 24(3):197-219; Skandan, et al., Nanostructured Materials 1999; 11 (2):149-158) are particularly well suited for producing nanoparticles of various oxides with controlled properties. Usually, metalorganic precursors are injected into a fuel/air mixture. The precursor materials decompose and the produced metals oxidize in a well-controlled flame yielding a uniform nano-sized oxide powder product. More recently, the formation of narrowly and specifically shaped nano-oxide particles or nano-fibers was achieved by flame synthesis performed over specifically prepared substrates introduced in well-controlled flat flames (Xu, et al., Applied Physics Letters 2006; 88(24) art. no. 243115). Alternatively, external electric fields can be used to control the formation of oxide nanoparticles and their agglomeration (Zhao, et al., Journal of Nanoparticle Research, 2007; 1-17).


Metal oxide nanoparticles customized for reactive nanocomposite materials were developed in (Prakash, et al., Nano Letters 2005; 5(7): 1357-60). Strong oxidizer nanoparticles (potassium permanganate) were coated with a layer of a relatively mild oxidizer (iron oxide). The composite oxidizer nanoparticles were synthesized by a new aerosol approach in which the nonwetting interaction between iron oxide and molten potassium permanganate aids the phase segregation of a nanocomposite droplet into a core-shell structure. The iron oxide coating thickness was varied to tune the reactivity of the product. Such core-shell engineered nanoparticles are promising for adjustment of the reaction rates in the nanocomposite energetic materials.


A wet chemistry approach is generally useful for preparation of nano-sized oxide particles suitable for energetic formulations. For example, a process for the preparation of nanosized tungsten oxide particles is described by Perry, et al., Propellants, Explosives, Pyrotechnics 2004; 29(2):99-105. In that process, ammonium paratungstate was dissolved in acid and the product, tungstic acid, was precipitated by addition of distilled water. The product consisted of 7 nm thick platelets of hydrated WO₃, with the plate length of about 100 nm. Such particles are useful for preparation of nanocomposite thermites.

Preparation of Reactive Nanocomposite Materials

Powder Mixing

metal powders are added just before the gelation while the solution is being stirred. The final step of removing the pore fluid from the system is accomplished by either controlled slow evaporation or by supercritical extraction with CO₂. Respectively, aerogels or aerogels are produced. To produce aerogel, prior to supercritical extraction, the liquid in the pores is replaced by CO₂ by a series of flush and drain cycles. Further functionalization of the oxide matrix is achieved using various silane additives (Clapsaddle, et al., Materials Research Society Symposium Proceedings 2003; 800:91-6). This approach is attractive as it naturally generates a very intimate mixing between the components. The disadvantages include: high porosity of the final composite makes it undesirable for some applications, restrictions on the types of materials that can be gelled, and a difficulty in scaling up the production rate—chiefly because of the need to introduce the metallic nanopowders in the stirred solution at a very specific stage of the gel preparation process.

Self Assembly

Recently, self-assembly approaches were considered to prepare reactive nanocomposite materials starting with nanosized aluminum powder and functionalized nanosized oxide particles (Gangopadhyay, et al., U.S. Pat. Appl. Publ. US 200705445 A1 20070503, 2007; Subramaniam, et al., Materials Research Society Symposium Proceedings 2006; 896:9-14; Apperson, et al., Applied Physics Letters 2007; 91, Article No. 243109; Mehenale, et al., Journal of Energetic Materials 2006; 24:341-60). To produce ordered assemblies, metal particles were arranged around the exterior surface area of oxide nanorods or in the ordered pore structure of the mesoporous oxidizer particles in composites. For example, the self-assembly in an Al—CuO system was achieved by initial functionalization of the CuO nanorods by applying a monofunctional polymer, poly(4)-vinyl pyridine (P4VP). The nanorods were prepared for these experiments using the surfactant-templating method. Al nanoparticles adhere to functionalized nanorods and these “decorated” nanorods become ordered within the material (Subramaniam, et al., Materials Research Society Symposium Proceedings 2006; 896:9-14; Apperson, et al., Applied Physics Letters 2007; 91, Article No. 243109). Such ordered structures are reported to produce higher flame speeds in small-scale laboratory evaluation tests compared to nanocomposite materials with the same compositions conventionally mixed using ultrasonic suspension. A conceptually similar approach was used to prepare self-assembled Al—Fe₂O₃ nanocomposite thermite (Mehendale, et al., Journal of Energetic Materials 2006; 24:341-60). A porous Fe₂O₃ was synthesized using a micelles template-assisted sol-gel synthesis route using surfactants. The addition of surfactants during sol-gel synthesis generates an ordered pore structure. A reference sample of porous Fe₂O₃ was also prepared by the same process but without the use of surfactants, so that the pore structure was not ordered. Both oxidizers were mixed with n-Al and the combustion rates were compared to each other. The ordered structure produced a higher flame speed. The ordered nanocomposites are attractive as offering a better control over the material properties and potentially higher reaction rates in practical applications. The shortcomings of this approach include the high costs of custom-made oxides, the presence of functionalizing agents which generally reduce the energy...
density of the energetic formulation, and the inherently high porosity of the produced materials.

**Layered Vapor Deposition**


Developed originally for joining applications (Wang, et al., 2003 *Applied Physics Letters* 83(19):3987-9; Wang, et al., *Journal of Applied Physics* 2004; 95(1):248-56; Dukham, et al., *Journal of Applied Physics* 2004; 96(4):236-42), reactive nanofilms attract more and more interest as energetic components. Most work has been reported for Ni—Al nanofilms, for which many reaction details were studied, including the effect of partial annealing resulting in an increased thickness of the partially reacted layer between bilayers of Al and Ni (Gavens, et al., *Journal of Applied Physics* 2000; 87(3):1255-63). Multilayer Al—Ni films were prepared using magnetron sputtering, by rotating a water-cooled brass substrate over fixed Al and Ni guns. The number of produced bilayers exceeded 4000. The thickness of individual bilayers varied from 25-80 nm. Substantial efforts were also made to prepare and characterize nanofilms of Al—CuO thermite (Blobaum, et al., *Journal of Applied Physics* 2003; 94(5):2915-22; Blobaum, et al., *Journal of Applied Physics* 2003; 94(5):2923-9).

CuO—Al nanofilms were similarly prepared by magnetron sputtering performed in argon at 5 mTorr. To avoid the reaction between CuO and Al, the sputter guns were shielded to contain the plasma in a small volume above each target. The substrate carousel was also water cooled to minimize mixing and reacting of the layers during deposition. The sputter-deposited CuO had the structure of the mineral parameleaeite, Cu_{2}O_{2}. Each thermite bilayer was 1 μm and the total foil thickness was 14 μm. Electron microscopy images of the prepared thermite nanofilms are shown in FIG. 11.

**Arrested Reactive Milling**

Current literature describes only one “top-down” approach for preparing reactive nanocomposite materials where the nano-sized structure is obtained by refining course starting materials. The nanocomposites are produced using a technique similar to mechanical alloying, called Arrested Reactive Milling (ARM) (Drezin, et al., US Patent Publication 20060053970, the disclosure of which is incorporated by reference herein; Schoenitz, et al., *Materials Research Society Proceeding* 2004; 800:AA2.6.1-6; Schoenitz, et al., *Proceedings of The Combustion Institute* 2005; 30:2071-8; Umbrjakar, et al., *Propellants, Explosives, Pyrotechnics* 2007; 32(1):32-41; Drezin, et al., *International Annual Conference of ICT* 2005, 36th (Energetic Materials), p. 138/1-138/12; Umbrjakar, et al., *Propellants Explosives and Pyrotechnics* 2006; 31(5):382-9; Umbrjakar, et al., *Journal of Propulsion and Power* 2008; 24(2):192-8). The starting materials are mixtures of regular metal, metalloid and/or oxide powders. The sizes of starting powders are not critical and using very fine or nanosized powders as starting materials is, in fact, undesirable. In order to produce reactive nanocomposites, starting components are selected among materials capable of reacting exothermically. Metals and metal oxides (thermites) represent one popular class of related compositions. Boron and metals such as titanium, zirconium, or hafnium forming respective borides represent another class of useful compositions. When powders of such materials are mixed and ball-milled, the exothermic reaction can be initiated mechanically. Once initiated, the reaction becomes self-sustaining. The reaction usually proceeds very rapidly resulting in substantial increases in both the pressure and temperature within the milling vessel. Reactive nanocomposites are produced when the milling process is interrupted (or arrested, hence ARM) just before the self-sustaining reaction is mechanically triggered. For small scale samples, preliminary experiments are used to establish the time when the self-sustaining reaction is triggered. For larger scale samples, the milling conditions and the time of milling are predicted using numerical modeling of energy transfer between the milling media and the powder (Ward, et al., *Acta Materialia* 2005; 53:2909-18).

ARM leads to the formation of fully dense, micron-sized composite particles with nanoscaled structural features. Each particle is a three-dimensional composite of starting materials as opposed to homogenized or chemically bonded compounds thereof. The milling time at which the reaction is mechanically triggered effectively sets a limit to the spatial scale on which the components are mixed. This time limit can be influenced by the specific milling parameters chosen—the powder batch size, the mass ratio of powder sample to that of the milling media, the processing temperature, and the use of process control agents. Collisions between the milling media subject the milled powder to transient pressures of up to 5 GPa (Suryanarayana, *Progress in Materials Science* 2001; 46(1-2):1-184), individual particles have therefore near theoretical maximum density (TMD).

ARM processing is very flexible and versatile. It does not have the many limitations of chemical or vacuum condensation techniques, which can be used only with selected compositions. It has been observed that essentially any combination of reactive materials can be processed by ARM to prepare a nanocomposite reactive powder. Table 4 lists all compositions prepared by ARM to date including multiple thermites and metal-metalloid systems. The process is readily scalable and inexpensive. One of the important limitations of the ARM processing is the inevitable presence of a fraction of reacted material in the prepared nanocomposite powder. Such reacted material forms in relatively small quantities during the processing when a reaction between the components is locally triggered mechanically but is not self-sustained within the sample. As a result, the small quantities
of the reaction products are redistributed and homogenized within the sample that is continued to be ball milled. The presence of the partial reaction products can be minimized by adjusting the milling conditions and parameters (Umbrajkar, et al., Propellants Explosives and Pyrotechnics 2006; 31(5): 382-9; Umbrajkar, et al., Journal of Propulsion and Power 2008; 24(2):92-8). The safety of the ball mill operation must be considered when preparing reactive nanocomposite materials by ARM. Specifically, the self-sustaining reaction between the reactive components must be prevented to avoid the damage to the processing equipment and facility.

<table>
<thead>
<tr>
<th>TABLE 4</th>
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<tbody>
<tr>
<td>Reactive nanomaterials prepared by ARM to date</td>
</tr>
<tr>
<td>Oxidizer</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>AlₓMg₁₋ₓO₃</td>
</tr>
<tr>
<td>MgH₂</td>
</tr>
<tr>
<td>Si</td>
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<tr>
<td>Zr</td>
</tr>
<tr>
<td>2B + Ti***</td>
</tr>
<tr>
<td>2B + Zr***</td>
</tr>
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</table>

| Reactive Metal-Metalloid composites |
| B | Reactive metals: Ti, Zr, Hf | Nanostructured Al-based alloys |
| Si | Reactive metal: Ti |

| Alloying components: W, Fe, Hf, Mg, MgHₓ, Ti, Li, Zr, C, I, Zn |

*Metal-rich nanocomposites also have been synthesized
**Metal-lean nanocomposites also have been synthesized
***Nanocomposite powder used as component for compound nanocomposites

[0074] A characteristic cross-section of a particle of an Al—CuO nanocomposite prepared by ARM is shown in FIG. 12. The inclusions of CuO in Al matrix vary in size from 1 μm down to less than 50 nm. It is important to note that inclusions of one component (e.g., CuO for the example shown in FIG. 12) are fully embedded into the matrix of the other component (e.g., Al). Therefore, the entire Al/CuO interface area will participate in the exothermic heterogeneous reaction upon thermal (or thermal) initiation of such a material. This would not be the case for a material prepared as a mixture of nanopowders in which the reactive particles only have direct contact over a relatively small portion of the total surface area of each nanosized component. The propagation mechanisms for the reactions in fully dense nanocomposites prepared by ARM and in the highly porous mixtures of nanopowders with identical bulk chemical compositions may be entirely different. The pores may play a critical role in promoting the pressure-driven reaction propagation, while a slower, thermal reaction propagation mechanism is expected for the fully dense nanocomposites.

[0075] Reactive milling has also been investigated in Russia to produce energetic compositions refined on the nanoscale termed Mechanically Activated Energy Composites (MAEC) (Dolgoborodov, et al., Khimicheskaya Fizika 2004; 23(9):85-9; Dolgoborodov, et al., JETP Letters 2005; 81(7):311-4; Dolgoborodov, et al., Khimicheskaya Fizika 2007; 26(12):40-5). Most of the effort focused on metal-Teflon compounds (Dolgoborodov, et al., Khimicheskaya Fizika 2004; 23(9):85-9; Dolgoborodov, et al., JETP Letters 2005; 81(7):311-4). Al, Mg, Ti, and Zr powders were used while major experiments focused on Al- and Mg-based composites (Dolgoborodov, et al., Khimicheskaya Fizika 2007; 26(12):40-5). Similar to the ARM approach, the milling conditions in a vibratory mill are selected to avoid or minimize the reaction between the components while achieving maximum degree of homogenization between the starting materials.

Materials Properties

[0076] Knowledge of material properties is essential for understanding their reaction mechanisms, for prediction of their performance in energetic formulations, and for designing practical systems and components employing such materials. Some of the material properties commonly used for micron-sized reactive powders and structures must be redefined for materials with nano-scale features. For example, many reaction features for conventional metal fuels are affected by such thermodynamic properties as melting and boiling point of the metals and their respective oxides. However, for material domains of nanometer dimension, the structure and phase stability are strongly affected by the surface energy. As a result, melting can occur at different temperatures for domains (particles or crystallites) of different sizes and may not be observed at all if the domains are sufficiently small, e.g., see (Tanaka, et al., Zeitschrift fuer Metallkunde/ Materials Research and Advanced Techniques 2001; 92(5): 467-72; Goldstein, et al., Science 1992; 256(5062):1425-7; Lai, et al., Physical Review Letters 1996; 77(1):99-102; Allen, et al., Thin Solid Films 1986; 144(2):297-308). The enthalpy of formation of respective nanodomains and their combustion enthalpies will also be altered compared to the coarser components with the same elemental compositions. Effects of surface energy on the boiling temperature and on the equilibrium vapor pressure as a function of temperature can also be significant (Farrell, et al., Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures—Processing, Measurement, and Phenomena 2007; 25(4): 1441-7). Similarly to thermodynamic properties, mechanical properties of nano-sized particles or surface layers coating such particles cannot be described using conventional characteristics for bulk materials (Misra, et al., Advanced Engineering Materials 2001; 3(4):217-22).

Particle Size Distributions, Surface Morphology, and Active Metal Content

[0077] The sizes of the nano-domains and the nanoparticles, are of primary importance in determining the rates of heterogeneous reactions commonly leading to ignition of such materials. Similarly, the particle size distributions and related specific surface values of nano-composite materials affect their aging characteristics, i.e., changes in the oxide layer thickness, partial reaction between components, etc. Particle sizes must be known to design appropriate material handling and mixing techniques. Because of the polydisperse nature of nanopowders and nanodomains observed in reactive nanocomposites, the quantitative descriptions of the respective particle size distributions are difficult to obtain. Agglomeration that can be very significant for nanopowders makes quantitative description of the particle distributions even more difficult. It should be noted that the combustion performance may be quite different for the powders with the same
specified prime diameters or even with similar size distributions for the primary particles if one of the powders is much more agglomerated than another. The agglomeration of nanopowders is unavoidable (Singhal, et al., *Nanostructured Materials* 1999, 11(4):545-52), while its detailed mechanisms and their correlation with other powder properties are poorly understood.

[0078] The problem of quantifying the particle size distribution for the nano-composite materials becomes even more challenging considering that at least two nano-sized phases are present. For the simplest case of aluminum nanopowder, the second phase is the passivating oxide (or any other) surface layer. For the more complex superthermals, intermetallic, or metal-metallloid composites, additional phases include various oxides, metals, alloys, and metalloids.

[0079] Various particle shapes introduce yet another layer of complexity in the quantitative particle size distribution measurements. Most particle sizing techniques implicitly assume that the particles are spherical in shape. Depending on the preparation technique, this assumption may or may not hold true for different aluminum nanopowders. The assumption of the spherical particle shape is most likely to be incorrect for oxide and metalloid nanoparticles. An approach for describing particle dimensions and shapes for non-spherical and highly agglomerated particles based on analysis of the powder fractal dimensions has been developed and used extensively for many agglomerated powders and aerosols (Kirdrangtenko, et al., *Environ. Sci. Technol.* 1994; 28:2197-202). Most commonly, textural and density (or structural) fractal dimensions of the aerosol particles are considered (Colbeck, et al., *J. Aerosol Sci.* 1997; 28:715-23; Colbeck, et al., *J. Aerosol Sci.* 1997; 28:715-23). This approach may prove to be useful for characterization of many non-spherical and agglomerated reactive nanopowders.

[0080] Substantial efforts were made to characterize aluminu nanopowders which serve as the most popular component of reactive nanomaterials. With advances in electron microscopy, imaging of the nanoparticle samples became a common practice. Results obtained from electron microscopy can be readily used for straight-forward, although labor-intensive, size classification of the observed particles, e.g., (Ermlone, et al., *Nanootechnology* 2002; 13:638-43). In order to be representative, such measurements must consider a large number of particles. It is also desired that the particle sizing be performed in different locations of the sample prepared for the electron microscopy. In addition to the direct measurement of the particle size distribution, electron microscopy provides very important information about the particle shapes, the thickness of the oxide layer (high resolution TEM), and about the particle surface morphology. This information is important for interpreting the results of various other particle sizing techniques based on light scattering, surface areas by gas absorption, etc.

[0081] The most common characterization of the particle size is obtained from the specific surface measurements. Usually, a BET (Brunauer-Emmett-Teller) measurement of gas adsorption is employed, e.g., (Puszynski, et al., *Materials Research Society Symposium Proceedings* 2006; 896:147-58; Moore, et al., *Journal of Propulsion and Power* 2007; 23(1): 181-5; Prentice, et al., *J. Phys. Chem. B* 2005; 109:20180-5) to obtain a single number characterizing the dimension of the specific nanopowder. The "BET diameter" is often introduced by assuming that the measured specific surface of a powder is equivalent to that produced by monodisperse spherical particles. For many applications this represents the single most important characteristic of a nanomaterial. A similar, "one number" assessment of the particle size can be obtained for nanopowders and for fully dense nanocomposite materials using broadening of the x-ray diffraction line and the well known Scherrer formula (Patterson, *Physical Review* 1939; 56(10): 978-82). Modifications of this approach have also been discussed in the literature to obtain a more accurate assessment of the nano-domain dimension (Hall, et al., *Journal of Applied Crystallography* 2000; 33(6): 1355-41). However, for many energetic materials, the width and shape of the particle size distribution are as important as any specific weighted average diameter, so that additional measurements are needed to obtain reliable particle size distributions.

[0082] Few commercial devices are available for sizing nanopowders. Submicron particle sizes can be quantified using low-angle laser light scattering and several commercial instruments utilizing this technique are available. These instruments are generally designed for size characterization of micron-sized powders and their range of measurements is extended to include particles as small as 40 nm with specific algorithms for processing the measured scattered laser emission. The main advantage of this type of measurement is that a powder with relatively broad particle size distribution can be characterized. However, for accurate measurements the optical properties of the material surfaces need to be known. Such properties are not well established for many materials, especially, for the nano-sized particles, for which, the material properties are expected to substantially differ from those of the respective bulk materials. Another group of devices uses photon correlation spectroscopy, which determines particle size by measuring the rate of fluctuations in laser light intensity scattered by particles as they diffuse through a fluid. The measurements need to be processed assuming a specific shape of the size distribution function, so that generally the mean particle size and the width of the particle size distribution can be quantified. For successful measurement, the powder needs to have a relatively narrow size distribution and the measurements become less and less useful as the width of the particle size distribution increases.

[0083] Currently, new approaches are being actively developed for characterization of the particle sizes of reactive nanomaterials. In one related approach, the particle size distributions are determined using thermo-gravimetric analysis (TGA) (Johnson, et al., *Journal of Propulsion and Power* 2007; 23(4):669-82). TGA measurement enables identification of the active metal content, e.g., the amount of un-oxidized aluminum for the Al nanopowder. In addition, the presence of volatile impurities can be detected and particle size distributions can be obtained. Interpreting the TGA curve, by considering the effect of particle oxidation of a pre-selected particle size, produces a measure of the primary particle size in the powder tested, similar to the gas absorption measurement. Comparison of TGA, BET, and SEM measurements of particle sizes, with the XRD analysis yielding a crystallite size, is presented by Johnson, et al., *Journal of Propulsion and Power* 2007; 23(4):669-82 for 12 different nano-aluminum samples. The results generally compare well to one another. However, for samples with the coarser particles implied by the TGA and SEM measurements, XRD did not show an appreciable increase in the crystallite sizes. In order to obtain particle size distributions, a curve-fit procedure is used to represent the experimental TGA curve as a superposition of "basic curves" that ideally represent the mono-
modal powder fractions. The basic curves are selected based on preliminary information about the specific nanopowder, e.g., obtained from SEM images. The main assumptions made were the shape of the particles (spherical), the thickness of the initial oxide layer, and the oxide density. Different alumina polymorphs have substantially different densities (Levin, et al., J. Am. Ceram. Soc. 1998; 81(8):1995-2012), so using an incorrect density for the starting “natural” alumina layer can cause a large error in the final particle size distribution. The TGA-based method was shown to be well suited for monitoring samples for the presence of larger, 0.5-5 μm diameter particles but ineffective for quantitative size distributions of powders containing particles smaller than 100 nm (Johnson, et al., Journal of Propulsion and Power 2007; 23(4):669-82). The main problem identified by Johnson, et al., Journal of Propulsion and Power 2007; 23(4):669-82 was the inconsistency in oxidation of various nanopowders at lower temperatures. This inconsistency was attributed to possible impurities in some of the nanopowders. In addition, particle coalescence during or after melting can occur resulting in the change of the particle sizes and respective differences in the oxidation behavior. Particles with dimensions greater than 10 μm impose another limitation because such particles may remain incompletely oxidized even at the highest temperatures (typically, 1500°C) achieved by TGA.

Another particle size measuring approach, suitable for many nanopowders or nanocomposite materials, involves small-angle X-ray and/or neutron scattering (SAXS, SANS) (Tranov, et al., Journal of Physical Chemistry B, 2006; 110(26):13094-9; Mang, et al., Journal of Materials Research 2007; 22(7):1907-20; Borchert, et al., Langmuir 2005; 21(5):1931-6). In refs. (Mang, et al., Journal of Materials Research 2007; 22(7):1907-20) and (Borchert, et al., Langmuir 2005; 21(5):1931-6), the results of SAXS and SANS measurements were shown to compare well to the results of electron microscopy, TGA, BET, and X-ray diffraction measurements. An example of such a comparison for SEM, SANS and SAXS results is shown in FIG. 13 (Mang, et al., Journal of Materials Research 2007; 22(7):1907-20). A detailed discussion of the underlying theoretical approach, as presented by Mang, et al., Journal of Materials Research 2007; 22(7): 1907-20, showing that specific information about the particle shape and morphology is needed in order to meaningfully process the scattering measurements. This information can be gained from detailed electron microscopy studies complementing the x-ray and neutron scattering measurements. Because x-rays and neutrons interact with matter differently, it is possible not only to quantify the particle size distributions, but also characterize the features of the composite particles. For example, the thickness of the oxide layers was evaluated with good accuracy based on the processed scattered intensity data (Mang, et al., Journal of Materials Research 2007; 22(7): 1907-20). In order to transform the scattering results into a size distribution, a specific model for the size distribution function must be assumed. In many cases (Tranov, et al., Journal of Physical Chemistry B, 2006; 110(26):13094-9; Borchert, et al., Langmuir 2005; 21(5):1931-6), the assumption of the lognormal distribution is well justified.

One of the more unconventional approaches used to size classify reactive nanopowders relied on a differential mobility analyzer (Jouet, et al., Chemistry of Materials 2005; 17(11):2987-96) well suited for measuring particle sizes for very fine airborne particles. Similar to the TGA technique, the assumptions about the thickness and density of the initial oxide layer (or impurities) affect the output substantially. Also well-suited for the nano-sized airborne particles is a technique described by Mukherjee, et al., Aerosol Science 2006; 37:677-695 and using quantitative laser-induced breakdown spectroscopy (LIBS). Qualitative LIBS was shown to be effective in finding the degree of oxidation of α-Al particles processed at different temperatures.

Generic SEM and TEM imaging techniques are invaluable for characterization of particle sizes, shapes, and surface morphology. High resolution TEM is successfully used to characterize the oxide coatings present on aluminum particles exposed to oxidizing environments. The information about thickness, crystallinity, microstructure, and homogeneity of the oxide layer is of critical importance for understanding the mechanisms of oxidation of metal nanoparticles. In turn, the mechanisms of oxidation affect both ignition and aging kinetics of many nanocomposite reactive materials. Most of the reports agree that the thickness of the oxide layer on the surface of aluminum particles is essentially independent of the particle size and is generally in the 2.5-3 nm range.

It is currently well established that the natural oxide layer on aluminum particles is amorphous. However, the images presented in FIG. 14 also show that the oxide coating is not homogeneous and includes precursors of the growing α-Al2O3 crystalline sheets. As shown in FIG. 14, these mismatching crystalline sheets can be exfoliated from the main amorphous film.

Characterization of composite materials is more difficult compared to elemental metal nanoparticles and much less progress has been made. For the materials prepared using starting nanosized powders, e.g., by mechanical mixing or sol-gel synthesis, the measure of the reactive surface is commonly obtained from the starting particle sizes. For the fully dense, nanocomposite materials, scanning electron microscopy of the cross-sectioned materials and XRD measurements of the crystallite sizes produce the data about the size distributions of the nanodomains, e.g., (Umbrakjark, et al., Propellants Explosives and Pyrotechnics 2006: 31 (5):382-9).

Finding the active (or metallic) Al content in powders is closely connected to the correct identification of the particle size, as already mentioned above. High resolution TEM images showing the thickness of the alumina layer combined with the data on the particle size distribution can be used to estimate either the volumetric or gravimetric fraction of pure Al in the powder. The active aluminum content can also be determined from TGA results by measuring the degree of powder oxidation upon heating. The above approaches all rely on assumptions about the density, structure, and homogeneity of the initial oxide layer. Yet, it has been reported that such layers can be porous, partially hydrated, somewhat non-uniform in thickness, or can contain some adsorbed gases (Ramaswamy, et al., Energetic Materials 2005; 23:1-25; Fedotova, et al., 36th Int. Annual Conference of ICT combined with the 32nd Int. Pyrotechnics Seminar, Karlsruhe, Germany, Jun. 28-Jul. 1, 2005, p. 147/1), all of which would affect the accuracy of the calculated available active metal content. The situation is complicated further for materials that are processed to produce specific passivating layers. Techniques that enable finding the active aluminum content for such cases include quantitative measurements of the gas evolved upon base hydrolysis (Johnson, et al., Journal of Propulsion and Power 2007; 25(4):669-82), chemical analysis using induced coupled plasma (ICP) emission to

Thermodynamics of Nano-Scaled Components

At the spatial scale of nanoparticles and nanodomains, thermodynamic properties of materials are altered. This includes changes in the melting point and latent heat of melting, which are of particular significance for reactive nanomaterials. In addition, phase transformations, such as polymorphic transitions between different aluminum oxide phases, are also affected by the reduced dimensions of the oxide films. Properties of other oxides or metals in other nanomaterials are affected similarly, but discussed much less in the literature.

The changes in the melting point for materials reduced to nano-sized particles or inclusions are extensively discussed in literature, e.g., Alcoutlabi, et al., J. Phys. Condens. Matter 2005; 17:R461-R524. This review of recent results showed that the Gibbs-Thomson model widely used to explain the depression of the melting point, Tₘ, is deficient at the nano-scale and further work needs to be done to fully capture size effects on melting behavior. In this review, the issue of depressed melting point is discussed in the context of its particular importance for reactive nanoparticles because melting is expected to substantially affect both ignition and combustion behaviors. Melting and oxidation of aluminum nanoparticles was recently systematically addressed by Trunov, et al. Journal of Physical Chemistry B, 2006; 110 (26):13094-9 and Rufino, et al., Acta Materialia 2007; 55:2815-27; Sun, et al. Thermochimica Acta 2007; 463(1-2):32-40) using differential scanning calorimetry. The main advantage of this approach is that the actual particle size distribution for each specific powder sample was obtained and used instead of the more commonly weighted average particle size or bulk value of the powder. The experimental particle size distributions were obtained using SAXS (Mang, et al., Journal of Materials Research, 2007; 22(7): 1907-20; Borchert, et al., Langmuir 2005; 21(5):1931-6). Two lognormal distributions were used to fit the experimental SAXS data for each analyzed nanopowder. While the shape of the size distributions was assumed, the mean modal diameters and widths of both lognormal distributions were varied to obtain the best fit with the SAXS measurement. The experimental particle size distribution functions were used to predict the differential scanning calorimetry (DSC) melting curves for different powder samples according to different models proposed for the melting depression as a function of particle size. These melting point models will be discussed briefly below.

A model describing the melting point depression and referenced in several recent papers dealing with aluminum nanopowders used in combustion systems, e.g. Hunt, et al., Acta Materialia 2004; 52(11): 3183-91; Hunt, et al., Intermetallics 2006; 14(6):520-9; Granier, et al., Combustion and Flame 2004; 138(4):373-83, was developed decades ago by Reiss and Wilson Reiss, et al., J. Colloid Sci. 1948, 3:551-61. The model describes the melting point, Tₘ, as a function of the particle diameter, Dₚ, and the oxide film thickness hₗ, as:

\[
Tₘ = Tₘ[1 - \frac{4\sigma_d}{k_B \mu_0 (D_p - 2hₗ)}]^{\frac{k_B}{2}}
\]

where Tₘ is the melting temperature of bulk aluminum (933.47 K or 660.32°C), kₜ is the enthalpy of fusion of bulk aluminum, and 4σ_d is the interfacial surface tension between the solid and the liquid. The difference in the molar volumes between solid and liquid aluminum was neglected.

More recently, a theoretical model for melting of nanocrystalline metal powders was developed by Jiang et al., (Reiss, et al., J. Colloid. Sci. 1948, 3:551-61; Jiang, et al., Materials Letters 2002; 56:1019-21; Liang, et al., Physica B 2003; 334:49-53; Zhao, et al., Solid State Communications 2004; 130:37-9). The melting point was suggested to depend on the diameter of aluminum nano-crystals, D, often assumed to be equal to the diameter of the aluminum core for the oxide-coated aluminum nanoparticles, as:

\[
Tₘ = Tₑ[\exp\left(-\frac{2Hₑ}{3k_B Tₑ (D/dₗ)}\right)]^{\frac{1}{2}}
\]

where R is the universal gas constant and l is the length of the Al—Al atomic bond. It was further suggested that for nanoparticles, the latent heat of melting, Hₑ, depends on the particle diameter as:

\[
Hₑ = Hₑ[\exp\left(-\frac{2Hₑ}{3k_B Tₑ (D/dₗ)}\right)]\left[1 - \frac{1}{(D/dₗ)}\right]
\]

Processing the experimental results reported by Eckert et al., (Eckert, et al., Nanosstructured Materials 1993; 2:407-13) for composite materials containing nanosized aluminum inclusions produces phenomenological dependencies for both the melting point (K) and latent heat of melting (kJ/mol) as functions of the aluminum core diameter (nm):

\[
Tₑ = 977.4 - \frac{1920}{D}
\]

\[
Hₑ = 14.705 + \frac{177.49}{D}
\]

Some experimental data limit the applicability of Eqs. (4, 5) to particles with diameters in the range of 12 nm<D<43 nm. For larger particles, Tₑ=Tₑ and Hₑ=Hₑ. For particles with the metal core smaller than 12 nm, the latent heat of melting is reported to be negligible (Eckert, et al., Nanostructured Materials 1993; 2:407-13). Free aluminum nanopowders with sizes less than 20 nm are not currently available, but the approach described by Sun, et al. Thermochimica Acta 2007; 463(1-2):32-40 enables direct experimental study of melting in such particles obtained by controlled oxidation of coarser starting powders.

The three different melting models introduced above, were used with the experimental PSD to quantitatively predict the DSC signals expected for melting of different commercial nanopowder samples. Each calculation was compared to a specific DSC run. Additional corrections for pos-
sible sample aging were made as described in detail by Trunov, et al. *Journal of Physical Chemistry B*, 2006; 110 (26): 13094-9. Equations (1), (2), and (4) give the functional dependence of the melting temperature on the particle diameter. These equations were converted into equations that give the functional dependence of the aluminum core diameter on the melting temperature, \( D \rightarrow \Delta T_m \). The converted equations, and their temperature derivatives

\[
\frac{\partial D}{\partial T_m}
\]

were used to predict the DSC signal directly. The DSC signal, \( \dot{Q} \), predicted for each specific temperature, \( T \), and each specific heating rate, \( b \), was calculated as:

\[
\dot{Q} = M_p \pi D^3 \frac{\partial P}{\partial T} D^3 H_m \frac{d D}{dT} \frac{d D}{dT}
\]

(6)

where \( P(D) \) is the normalized frequency function, of aluminum nanoparticle distributions obtained from SAXS measurements and \( M_p \) is the normalization parameter for \( P(D) \) accounting for the aluminum metal mass in the analyzed sample.

Comparisons of the experimental DSC melting curves with the predicted DSC curves from these models are presented in FIG. 15. There is no close agreement between the experimental DSC curve and any of melting model predictions; however, the overall shape of the melting enthalpy was predicted by all the models. In particular, it is interesting that the experimental enthalpies have at least two peaks and this overall shape is generally predicted considering the bimodal size distributions obtained from SAXS. According to Eqs. (4, 5) (Eckert, et al., *Nanostructured Materials* 1993; 2:407-13), only a fraction of the powder is predicted to melt below \( T_m \). The rest of the powder, as noted in FIG. 15, is expected to melt at a constant temperature of \( T_m \) so that respective calculations for the melting enthalpies could not be performed and are not shown in FIG. 15.

Trunov, et al., *Journal of Physical Chemistry B*, 2006; 110(26): 13094-9 found that the shapes of the predicted curves are very sensitive to the specific type of the particle size distribution, e.g., bimodal vs. single mode lognormal distribution. The melting curves can further depend on the specific surface morphologies of the used nanoparticles that could affect the sizes of melting nano-domains. Independent experiments (Trunov, et al., *Journal of Physical Chemistry B*, 2006; 110(26): 13094-9; Rufino, et al., *Acta Materialia* 2007; 55:2815-27; Sun, et al. *Thermochimica Acta* 2007; 463(1-2): 32-40) confirm that the melting of aluminum nanopowders starts at a lower temperature than the melting point of bulk aluminum; however, existing models describe the effect of the particle size on the melting point depression only qualitatively. Detailed analysis of the particle size distributions and surface morphology is needed for quantitative verification of any related models.

The thermodynamic parameters of oxides or other nano-scale material components used in reactive nanocomposite materials have not been discussed in the literature dealing with reactive materials and their applications. At the same time, reducing the crystallite or particle size to the nano-scale certainly affects the thermodynamic properties and the stability of oxides, hydroxides, and other related compounds, e.g., see reviews (Navrotsky, *Mineralogy and Geochemistry* 2001; 44:73-103; Navrotsky, *Geochemical Transactions* 2003;4(6):34-7). The lack of attention to such effects in the community dealing with reactive and energetic materials is most likely due to fact that the reaction enthalpies in the systems of interest (e.g., thermitites) are much greater than the anticipated effects of fine particle sizes on the enthalpy of formation or surface energy. On the other hand, often the reaction rates in nanocomposite materials are limited by the diffusion of fuel and/or oxidizer through the growing or decomposing oxide layers. Thus, the properties of such layers determine the diffusion and respective reaction rates. A relevant example is the recently developed aluminum ignition model in which the rate of aluminum oxidation is calculated as a function of oxide layer thickness and, most significantly, the polymorphic modifications in the aluminum oxide layer present on the particle surface (Trunov, et al. *Combustion and Flame* 2005; 140(4): 310-8; Trunov, et al. *Combustion Theory and Modelling* 2006; 10(4):603-23). Polymorphic transformations occur in alumina as a function of both temperature and thickness of the oxide film (Jeurgens, et al., *Phys. Rev. B* 2000; 62(7):4707-19), while the rates of diffusion through different alumina polymorphs differ substantially. In addition, polymorphic phase changes in alumina are accompanied by substantial density change, so that the thickness and continuity of the oxide layer and thus the oxidation rate can be dramatically affected by such transitions, even though the transition energy is negligible compared to that of aluminum oxidation heat release. In another relevant case, many important thermite reactions occur through formation of multiple intermediate phases. Likewise, for the 2Al + MoO_3 → Al_2O_3 + Mo reaction to occur in the solid state (at relatively low temperatures), based on the Mo–O phase diagram, molybdenum oxide is likely to form a number of oxides, MoO_3→MoO_2→MoO_1→MoO_2 before being reduced to metallic Mo. When the initial MoO_3 particle or inclusion is of the nano-dimension, the stability of different produced suboxides can be affected and, respectively, the sequence of the phase changes can be altered compared to that implied by the known phase diagrams developed for bulk materials. Therefore, the reaction mechanism in such thermite systems may depend on the dimensions of the initial oxide particles and layers. Detailed studies of the stability of and phase transitions in various nano-scaled oxides used in reactive nanocomposite materials are thus needed for the mechanistic understanding and modeling of the heterogeneous reactions in such materials.

**Exothermic Heterogeneous Reactions**

The exothermic heterogeneous reactions both drive ignition and affect aging of reactive nanomaterials. Among such reactions, oxidation of nano-aluminum is the most fundamental and occurs in all such materials containing aluminum. This oxidation process was recently studied extensively and its mechanisms continue to be the subject of considerable debate.

**Aluminum Oxidation in Gaseous Oxidizers**

The primary experimental technique used for studies of oxidation of n-Al in oxygen-based, vapor phase oxidizers is thermal analysis. TGA curves show the sample weight

[0102] The TGA results presented above are generally inconsistent with a set of data obtained using single particle mass spectrometry (SPMS) (Park, et al., J. Physical Chemistry B. 2005; 109(15):7290-9; RAI, et al., J. Phys. Chem. B 2004; 108:14793-5). Unlike TGA experiments, SPMS measurements are performed on individual nanoparticles. The nanoparticles are either generated within the experimental setup by laser or arc ablation of an aluminum target or from commercial powders fed into the apparatus from a methanol suspension. The particles are passed through a furnace with a section heated to a target temperature and then fed into the SPMS analyzer. Characteristically, the heated section is 30 cm long and the typical exposure time is 1 s. In the analyzer, the particles are fed into a powerful laser beam ensuring the complete ablation and ionization of all particles. The produced ions are sampled with a linear time of flight mass spectrometer. Thus, the abundances of aluminum and oxygen atoms are obtained and the differences between particles with different degrees of oxidation are identified.

[0103] The SPMS results detect substantial oxidation only above the melting point of aluminum. These results were found to be in quantitative agreement with the hot-stage TEM observations also reported by RAI, et al., J. Phys. Chem. B 2004; 108:14793-5. The TEM imaging showed pronounced changes in morphology and evidence of aluminum leaking out from the oxide shell once the aluminum melting point was exceeded. Park, et al., J. Physical Chemistry B. 2005; 109(15):7290-9 and RAI, et al., J. Phys. Chem. B 2004; 108:14793-5 argue that their results are more accurate than TGA measurements (which they also performed obtaining results consistent with other published TGA experiments (Park, et al., J. Physical Chemistry B. 2005; 109(15):7290-9)). The main proposed reason for the improved accuracy is that single, non-interacting particles are studied in the SPMS experimental configuration while particle interaction within the TGA sample could cause heating of the sample above the controlled TGA furnace temperature.

[0104] Review of multiple references describing similar TGA measurements for oxygen absorbed wide range of aluminum powders suggests that the interaction of the particles in TGA experiments resulting in a measurable sample overheating causing an accelerated oxidation is unlikely. Consistent TGA observations have been reported for different powder samples treated in different instruments and using different sample holders and sample masses. Furthermore, the same reaction rates were observed in isothermal experiments (Jones, et al., Journal of Thermal Analysis and Calorimetry 2000; 61(3):805-18). Note also that the overall oxidation sequence including low-temperature oxidation steps distinguished clearly in the TGA experiments was observed for powders with a wide range of particle sizes, including 10-14 μm spherical powders (Trunov, et al., Combustion and Flame 2005; 140(4): 310-8; Trunov, et al. Combustion Theory and Modelling 2006; 10(4):603-23), for which self-heating due to oxidation at low temperatures is expected to be negligible based on their relatively small specific surface area.

[0105] The reduced rates of oxidation implied by the SPMS experiments could have been affected by the following two issues. The first issue has to do with the sensitivity of the SPMS measurement and its capability to quantify the amount of oxygen present in aluminum particles coated by natural, 2-3 nm thick oxide layers. Park, et al., J. Physical Chemistry B. 2005; 109(15):7290-9 teach that the method should be sensitive enough to detect a 1-2 nm oxide coating on aluminum nanoparticles. Despite that, no oxide was detected for a commercial aluminum nanopowder while such powders always contain 2-3 nm natural oxide layers. A clear demonstration of the sensitivity of the SPMS technique is therefore needed that would indeed show the presence of the 2-3 nm oxide coating present on commercial nanoparticles, for which the presence of the oxide coating has been established by TEM or another appropriate technique. The second issue is that in the experiments of Park, et al., J. Physical Chemistry B. 2005; 109(15):7290-9 and RAI, et al., J. Phys. Chem. B 2004; 108:14793-5, the particles were subjected to a temperature ramp before entering the furnace section heated to the target temperature. Because the entire particle feed system was filled with an oxidizing gas, the heating ramp could substantially passivate (oxidize) the particles resulting in the formation of a thicker and thus more protective oxide layer than exists on the starting particles. Based on the reported experimental conditions, it is estimated that the particles approaching the test section at the pre-set temperature, were subjected to the elevated temperatures for a time period close to 1 s. Thus, the formation of a protective oxide film was inevitable for the nanoparticles produced in situ before these particles entered the test section pre-heated to the target temperature. For the commercial nanoparticles with the initial protective
oxide layer, the oxidation in the heating ramp section of the apparatus would be comparable to that occurring in the calibrated test section. This issue is critical for the particles generated in situ by arc or laser ablation, for which the passivation of the bare aluminum surface during the heating ramp can occur very rapidly. Thus, it is expected that both commercial and in-situ prepared nanoparticles could have been similarly partially passivated prior to entering the furnace section. Therefore, the measured reaction rates in both cases characterize aluminum nanoparticles with initial passivating oxide coating.

[0106] Aluminum oxidation has been studied using a differential mobility analyzer to measure the density of aluminum particles subjected to different temperatures in the oxidizing environment (Rai, et al., Combustion Theory and Modelling 2006; 10: 843-59). The oxidized particles were also examined using a TEM. It was found that particles exposed to a temperature exceeding 1000 °C become hollow. Based on those observations, it was proposed that at low temperatures, the rate of oxidation is controlled by inward diffusion of oxygen; above the aluminum melting point, the rate is controlled by aluminum outward diffusion. Thus, the oxidation was proposed to occur in two distinct regimes, responsible for the slow and fast oxidation occurring before and after aluminum melting, respectively. It was suggested that the conventional thermal analysis techniques are characterizing slow processes occurring in the time scale of minutes while the SPMS measurements presented by Park, et al., J. Physical Chemistry B 2005; 109(15):7290-9 and Rai, et al., J. Phys. Chem. B 2004; 108:14793-5 probed a much faster process completed within 1 s (Rai, et al., Combustion Theory and Modelling 2006; 10: 843-59). The difference in time scales involved with thermal analysis and SPMS measurements is certainly real and substantial. In fact, the time scales characteristic of the most practical applications of related energetic nanomaterials are much shorter than those used in both techniques. Generally, the longer the time scales involved with a specific experimental technique, the easier it is to overlook a short-duration process. At the same time, such short duration processes can only be meaningfully detected and described by studies of the same material systems at the systematically varying time scales.

[0107] An increase in the aluminum oxidation rate at higher temperatures (Rai, et al., Combustion Theory and Modelling 2006; 10: 843-59) is certainly observed in all experiments and is in agreement with the concept of the oxidation reaction rate controlled by mass transfer processes. However, the distinct transition from one oxidation regime to another upon aluminum melting is not detected in many TGA measurements that show no increase in the oxidation rate upon aluminum melting. A short-lived change in the oxidation mechanism detectable by SPMS but not by TGA could be associated with a rapid change in the oxidation rate (e.g., caused by discontinuities or cracks in the passivating oxide layer) followed by a particle self-heating and, therefore, sustained higher oxidation rates. In TGA experiment, the self-heating of the sample is effectively suppressed that would minimize the effect of a short duration process.

[0108] A systematic study of aluminum oxidation using TGA and analysis of the samples pre-oxidized to and recovered from specific temperatures was presented by Trunov, et al. Combustion and Flame 2005; 140(4):310-8; Trunov, et al. Combustion Theory and Modelling 2006; 10(4):605-25; Trunov, et al. Journal of Physical Chemistry B. 2006; 110 (26): 13094-9. As noted above, these TGA results are in agreement with many other TGA measurements reported elsewhere. From XRD analysis of the samples recovered from specific oxidation temperature conditions, it was established that different Al2O3 polymorphs are observed during different oxidation stages. A diagram in FIG. 17 shows a characteristic thermo-gravimetric analysis (TGA) curve of oxidizing aluminum powder (with micron-sized particles) and the sequence of changes in the alumina scale growing on the particle surface. The entire oxidation process is divided into four stages and specific processes occurring during each stage are illustrated schematically. The natural amorphous alumina layer covering the particle initially grows slowly during the low-temperature oxidation—Stage I. The energy of the oxide-metal interface stabilizes the amorphous oxide at low temperatures and only up to a critical thickness of about 5 nm (Levins, ASM Intl. 1998; Jeurgens, et al., Thin Solid Films 2002; 418:89-101). When the critical thickness is approached or when the temperature becomes sufficiently high, the amorphous oxide transforms into γ-alumina. The density of γ-alumina exceeds that of amorphous alumina (Levin, et al., J. Am. Ceram. Soc. 1998; 81(8):1995-2012), and the smallest observed γ-alumina crystallites have a size of about 5 nm (Dwivedi, et al., Journal of Materials Science Letters 1985; 4:331-43). Thus, if prior to the phase change the thickness of the amorphous layer was less than 5 nm, the newly formed γ-Al2O3 crystallites no longer form a continuous coverage for the aluminum surface. As a result, the rate of oxidation increases rapidly at the beginning of stage II as shown in FIG. 17. For nanoparticles, this can result in the complete or nearly complete oxidation (see FIG. 16). For larger particles, the openings in the oxide coating heal only after a small fraction of the metal is oxidized. Upon healing, the rate of oxidation decreases.

[0109] Based on the TGA trace shown in FIG. 17, no detectable mass increase occurs upon aluminum melting. Eventually, a regular polycrystalline layer of γ-Al2O3 forms by the end of stage II. The growth of γ-Al2O3 continues in stage III for which the oxidation rate was reported to be limited by the inward grain boundary diffusion of oxygen anions (Jeurgens, et al., J. Appl. Phys. 2002; 92:1649-56; Riano, et al., Acta Materialia 51: 3617-3634). Growth of the γ-Al2O3 layer can be accompanied by phase transformations into other transition polymorphs, such as δ-Al2O3 and θ-Al2O3, which have densities very close to that of γ-Al2O3 (Levin, et al., J. Am. Ceram. Soc. 1998; 81(8):1995-2012). Such transitions are not expected to affect the oxidation rate significantly. Other processes are largely irrelevant for powders or materials with aluminum nanodomains, which are oxidized completely well before the alumina layer becomes unstable. However, for completeness, the processes occurring at higher temperatures are reviewed briefly. Stage III ends when the increased temperature destabilizes the transition between alumina polymorphs. The particles stabilize at elevated temperatures and still denser a-alumina polymorph starts forming by the end of stage III. Thus, strictly speaking, stage III can be further broken down into three separate sub-stages: growth of γ-Al2O3, transformations to δ and θ alumina polymorphs, and transformation to a denser α-Al2O3 polymorph. Stage IV is considered to start when the oxide scale is completely transformed to α-alumina. When the initial α-Al2O3 crystallites form at the end of stage III, the thickness of the γ-Al2O3 layer decreases, and the oxidation rate increases momentarily. When most of the oxide layer is trans-
formed to the coarse and denser α-Al₂O₃ crystallites, resulting in continuous polycrystalline coverage, grain boundary diffusion processes slow down and the oxidation rate decreases rapidly.

[0110] Trunov, et al. *Combustion Theory and Modelling* 2006; 10(4):603-23) report the kinetic relations for the polymorphic phase changes occurring in alumina films coating aluminum powders determined from TGA experiments. Thus, a quantitative description of aluminum oxidation in gaseous oxygen for particles and domains of different sizes was obtained.

Reactions Between Condensed Components

[0111] Three main types of related reactive systems include thermite, intermetallic, and metal-metalliod compounds. Among these three classes of composites, reactions in thermites are of most interest for energetic materials applications and they have attracted the most attention in the research community. Reactions mechanisms in highly exothermic metal-metalliod systems (e.g., B–Ti or B–Zr nanocomposites) are among the least studied. Therefore, the discussion below focuses primarily on the reactions in thermitites.

[0112] The sequence of processes occurring in aluminum oxide and affecting aluminum oxidation in gaseous oxygen described above is expected to remain generally valid for aluminum reactions with various oxidizers, including metal oxides in nanocomposite thermitites. Clearly, the kinetic parameters of individual processes are expected to be affected. The stability ranges of different alumina polymorphs can also change as a result of presence of other metals or oxides. Formation of alloys or ternary oxides can result in even more complex and multistage reactions. For thermitites, reduction of metal oxides most often does not occur in one step; for example, as noted above, it is reasonable to expect that MoO₃ reduction to Mo occurs through formation of Mo₅O₁₇, Mo₅O₁₃ and MoO₂ according to the Mo—O phase diagram (Levinsky, *ASM Int.*, 1998). Formation of each individual sub-oxide is expected to alter the reaction kinetics. Current research is primarily aimed at quantitative experimental characterization of these more complex reaction mechanisms.

[0113] Thermal analysis remains the most important tool in studying reactions in thermite-type nanocomposites and in nanocomposite materials employing other types of exothermic solid-solid reactions. While the nano-dimensions themselves may not necessarily result in new reaction mechanisms, the exothermic processes that occur very slowly and remain undetected for coarser materials can become dominant ignition triggers for nanocomposite materials with the identical bulk compositions. In fact, DSC and DTA measurements for many nanocomposite materials detect reaction onsets at low temperatures and will be useful in characterizing the respective reaction kinetics. Despite many advantages, the thermal analysis techniques are poorly suited for detecting short-lived processes that might result in self-heating for individual particles or small samples. Straightforward extrapolation of the kinetic behavior observed in thermo-analytical experiments to much shorter time scales is not meaningful. Instead, reaction mechanisms identified from detailed thermo-analytical studies combined with other experimental techniques should be elucidated and used to predict the reactions occurring in practical applications.

[0114] Reactions in aluminum-copper oxide nanofoils, produced by magnetron sputtering, were studied in a series of experiments presented in refs. (Blobaum, et al., *Journal of Applied Physics* 2003; 94(5):2915-22; Blobaum, et al., *Journal of Applied Physics* 2003; 94(5):2923-9). Differential thermal analysis was used in addition to TEM and Auger profiling of the partially reacted samples. The preparation of multilayered thermitic nanofoils involves elevated temperatures so formation of pure CuO was not possible. It was reported that the sputter-deposited copper oxide had the structure of the mineral parameclonite, Cu₂O. The Al/Cu₂O molar ratio in the foils is approximately 2.5, so that based on the final products of Al₂O₃ and Cu, the system is somewhat aluminum-rich. Furthermore, aluminum was partially oxidized and copper oxide was partially reduced during the deposition so that that Al and Cu₂O bilayers with combined thickness of about 1 μm were separated by approximately 100 nm thick interface layers in which the concentrations of components were continuously changing, as was confirmed by the Auger profiles of Al, Cu, and O (Blobaum, et al., *Journal of Applied Physics* 2003; 94(5):2915-22). A narrow region of the interface was identified as an amorphous or nanocrystalline Al₂O₃.

[0115] DTA analysis showed that the exothermic reaction in such nanofoils occurred in two steps, with the peaks around 625°C (890K) and 835°C (1110K). Based on the DTA trace presented by Blobaum, et al., *Journal of Applied Physics* 2003; 94(5):2915-22; Blobaum, et al., *Journal of Applied Physics* 2003; 94(5):2923-9), and reproduced here as a dashed line in FIG. 18, the onset of an exothermic reaction can be assigned to about 500 K. There is a broad exothermic shoulder beginning at about 470°C (about 745 K) in addition to the two large peaks mentioned above. Based on detailed XRD and Auger studies of the samples quenched before the first exothermic peak, the authors concluded that most of the parameclonite was transformed into a mixture of CuO and Cu₂O. Based on further analyses of the partially reacted foils, likely rate-determining processes for each of the two reaction steps were proposed. In the first exothermic reaction, the lateral growth of Al₂O₃ nuclei was proposed to control the reaction rate. The reaction ended when a continuous Al₂O₃ layer was formed. Note the similarity of the temperature ranges for the end of this reaction step described in (Blobaum, et al., *Journal of Applied Physics* 2003; 94(5):2923-9) and the end of aluminum oxidation step II illustrated in FIG. 17, which was also assigned to the formation of a continuous γ-Al₂O₃ layer (Trunov, et al., *Combustion and Flame* 2005; 140(4):310-8; Trunov, et al., *Combustion Theory and Modelling* 2006; 10(4):603-23). The second exothermic peak for the Al—CuO nanofoils was proposed to be controlled by either diffusion of O through the Al₂O₃ or by thickening of the CuO product by a nonuniform reduction in copper oxide serving as the oxygen source. This interpretation is again consistent with that discussed in refs. (Trunov, et al., *Combustion and Flame* 2005; 140(4):310-8; Trunov, et al., *Combustion Theory and Modelling* 2006; 10(4):603-23) for aluminum, where the respective oxidation step was proposed to be controlled by the diffusion-controlled growth of γ-Al₂O₃.

[0116] Reactions in a similar Al—CuO nanocomposite material prepared by ARM were studied by Umbrajkar, et al., *Thermochimica Acta* 2006; 451:34-43. The bulk composition was stoichiometric, i.e., 2Al·3CuO and detailed DSC studies accompanied by XRD analysis of the samples oxidized to different temperatures were reported. A DSC trace from Umbrajkar, et al., *Thermochimica Acta* 2006; 451:34-43 is directly comparable to that presented in (Blobaum, et al., *Journal of Applied Physics* 2003; 94(5):2915-22; Blobaum,
et al., *Journal of Applied Physics* 2003; 94(5):2923-9)—shown in FIG. 18. The onset of exothermic reactions for the ARM-prepared material occurs at a noticeably lower temperature and the low-temperature shoulder is resolved to include at least two broad peaks. Only one of the two higher temperature peaks observed for nanofoils (Blaubum, et al., *Journal of Applied Physics* 2003; 94(5):2915-22; Blaubum, et al., *Journal of Applied Physics* 2003; 94(5):2923-9) is reported for the nanocomposite powders (Umbrajkar et al., *Thermochimica Acta* 2006; 451:34-43), for which the temperature scan was stopped at 1013 K (740° C.). In addition, two weak endothermic peaks are observed between 800 and 900 K, corresponding to the eutectics with CuAl2 and Cu4Al5, respectively. The presence of intermetallic phases in the reaction products was confirmed by XRD. Both the better resolved low-temperature shoulder and the formation of intermetallic phases in the Al—Cu system (requiring the presence of metallic Cu), suggest a substantially greater reaction rate at low temperatures for materials prepared by ARM as compared to the nanofoils. Because of the higher rate, a greater fraction of the copper oxide is reduced at the same temperatures for the ARM-prepared materials. The metallic copper formed is then capable of reacting with aluminum and producing the observed intermetallic phases. This enhancement of reactivity for the ARM-prepared materials compared to respective nanofoils can be explained by two main factors. First, the magnetron sputtered copper oxide was partially reacting with aluminum during its deposition and the initial phase of the deposited copper oxide was partially reduced. Second, the spatial scale of mixing between the metal and the copper oxide in the nanofoils was likely coarser than in the three-dimensional nanocomposite particles produced by ARM.

[0117] Studies of the partially reacted samples recovered from different temperatures presented by Umbrajkar et al., *Thermochimica Acta* 2006; 451:34-43 were inadequate to propose a specific reaction mechanism corresponding to the complex DSC pattern. It was clear that the reduction of CuO occurred through formation of Cu2O followed by the formation of Al—Cu alloys and metallic copper. Produced aluminum oxide phases were poorly crystalline and only weak peaks of γ-Al2O3 were detected in the XRD patterns of the partially reacted samples. Thus, instead of proposing a specific reaction mechanism, the reaction was simply presented as a superposition of at least four overlapping individual reactions. For each individual contribution, the generic reaction type was selected and activation energy was estimated specified by matching experimental DSC results collected at different heating rates.

[0118] Similarly to reactions for Al—CuO thermites, reactions for Al—MoO3 thermites were studied using thermal analysis for nanocomposite materials prepared by different techniques. DSC curves for stoichiometric 2Al+MoO3 prepared by ARM (Schoenitz et al., *Journal of Propulsion and Power* 2007; 23(4):683-7) and for a mixture prepared by ultrasonication of nanosized Al and MoO3 powders at the equivalence ratio of 1.2 (Sun, et al., *Thermochimica Acta* 2006; 444(2): 117-27) are shown in FIG. 19. The equivalence ratio for the ultrasonicated nanopowders was selected based on earlier experiments (Grauer et al., *Combustion and Flame* 2004; 138(4):373-83) showing the maximum reactivity of the respective nano-thermite prepared at that equivalence ratio.

[0119] Comparison of the DSC traces shown in FIG. 19 to each other shows that the exothermic reaction starts at lower temperatures and occurs more actively for the materials prepared by ARM. In both cases, the exothermic features are broad and individual peaks are difficult to separate. A closer inspection of the traces shown in FIG. 19 indicates that the DSC trace for the ARM-produced material could be constructed by overlapping the trace observed for the mixed nanopowders, with an additional, very broad exothermic feature starting at about 500 K and monotonously increasing up to about 900 K. Without specifying the reaction mechanism, the DSC traces for ARM-prepared materials were proposed to be modeled as a superposition of four overlapping reactions. Three of these reactions described individual smaller peaks, similar to those detectable from the DSC trace for mixed nanopowders. Each of these three peaks was described as a first order reaction, with the activation energies of 209, 211, and 373 kJ/mol, respectively (Schoenitz et al., *Journal of Propulsion and Power* 2007; 23(4):683-7). The fourth, broad feature, not detectable for the mixed nanopowder samples, was approximated by a low activation energy (90 kJ/mol) Jander type reaction commonly describing 3-dimensional diffusion. Note that the activation energy for the strongest peak observed was about 240 kJ/mol. Based on the DSC traces recorded at the same heating rate and shown in FIG. 19, for the ARM-prepared materials this peak is located between the third and fourth identified peaks, for which respective activation energies were 211 and 373 kJ/mol, respectively (Schoenitz et al., *Journal of Propulsion and Power* 2007; 23(4):683-7).

[0120] The mechanisms of these and other exothermic reactions in nanocomposite reactive materials are complex and involve a number of overlapping exothermic processes. Two fundamentally different approaches are possible to describe such reactions. One approach is based on understanding the individual processes occurring in the reacting materials. Such understanding is only possible based on complex investigations involving various material probing techniques combined with thermal analysis. The only example of this approach is reported by Blaubum et al., *Journal of Applied Physics* 2003; 94(5):2915-22; Blaubum et al., *Journal of Applied Physics* 2003; 94(5):2923-9 for thermitite nanofoils.

[0121] Reactions in intermetallic systems have been studied for many years and good reviews of the current approaches and understanding can be found in the literature, e.g., (Mehrer, JIM 1996; 37(6):1259-80; Lauria et al., *Materials Science and Engineering R: Report* 2005; 49(1-2):1-60; Morsi, *Materials Science and Engineering A* 2001; 299(1-2):1-15). The research is focused on understanding of the combined processes of diffusion, formation of solid solutions, and the formation of the intermetallic compounds. One of the most reactive intermetallic systems is Al—Ni and despite extensive previous studies (Morsi, *Materials Science and Engineering A* 2001; 299(1-2):1-15), the reaction mechanisms in this system remain the subject of debate. This reaction was recently studied for nanofoil materials (Blaubum et al., *Acta Materialia* 2003; 51:3871-84). The mechanism of the Al—Ni reaction is complex and includes formation of multiple intermediate phases, so that detailed studies combining thermal analysis with recovery and characterization of samples heated to intermediate temperatures, are extremely useful. The simple morphology of the nanofoils combined with a large reactive interface area enabled researchers to
observe and study reaction steps that are difficult to characterize for other types of composite materials. Different phases (e.g., Al₆Ni₁₅, Al₄Ni) were observed to form as the first intermediate reaction product in the bilayers of different thicknesses, which may reflect the effect of nanoscale dimensions on the thermodynamic stabilities of different compounds—mentioned above.

Ignition Studies

[0122] The exothermic heterogeneous reactions are responsible for ignition of reactive nanocomposite materials under practically useful conditions. The salient feature of ignition is that the materials are heated rapidly with powerful heat sources, such as a detonation front produced by an ignition primer or as an expanding fireball generated by a high explosive. Respective heating rates are of the order of 10⁶-10⁷ K/s. Thus, experimental validations of the ignition models must generate comparable heating rates while enabling controllable and reproducible conditions and accurate ignition detection.

[0123] In addition to reproducing the high heating rate, the entire nanocomposite should be heated and ignited in the ignition experiment, as opposed to selective heating (and possible volatilization or decomposition) of one component, which could result in different reaction kinetics. The uniform heating of composite material is readily achieved in thermoanalytical experiments with very low heating rates, but may present a challenge when the heating rates increase. Finally, for materials prepared as mixed nanopowders, the sample porosity can vary widely between experiments which could also substantially change the ignition behavior.

[0124] Lasers offer the capability of readily adjustable and well-controlled energy transfer to reactive materials with the range of power necessary to achieve the heating rates of interest. Lasers are now commonly used for laboratory studies of material ignition, e.g., (Dimitriou et al., AIChE Journal 1989; 35(7): 1085-96; Zakhvor, I., Izvestiya Akademii Nauk SSSR, Seriya Fizicheskaya 1991; 55(6): 1198-201; Fetherolf et al., Proceedings of the 16th International Pyrotechnics Seminar, 1991, p. 675-90; Kuo et al., Combustion and Flame 1993, 95(4):351-61; Ahmad et al., Propellants, Explosives, Pyrotechnics 2001; 26(5):235-45; Ali et al., Combustion Science and Technology 2003; 175(8):1551-71). Most significant issues for the nanocomposite materials are the consistency in the sample preparation and differences in efficiency of absorption of the laser energy by different material components (e.g., metals versus oxides or particles of different sizes present in the material). The efficiency of absorption of the near-infrared and visible spectra by nanoparticles of Al and B embedded in nitrocellulose or Teflon oxidizers was studied by Yang et al., Propellants, Explosives, Pyrotechnics 2005; 30(3):171-7. It was found that absorption strength is greater for Al nanoparticles as compared to bulk Al. A different experimental approach was used to assess the scattering and absorption efficiency of n-Al and nanosized MoO₃ powders (Begley et al., Journal of Heat Transfer 2007; 129(5):624-33). It was found that close-packed nanopowder of MoO₃ scatters most of the incident light while about 2/3 of the incident light are absorbed in a similarly packed n-Al. The experimental approach used in (Begley et al., Journal of Heat Transfer 2007; 129(5):624-33) required preparation of a 1-D slab with a moderate optical thickness, which proved to be difficult for n-Al.

while the same thermites prepared with the micron-sized powders were reported to ignite at 610°C. As reported earlier in the same article, ignition for both types of samples was detected optically using a high speed video camera. Without a very sensitive IR detector, however, optical emission is extremely hard to detect at 100°C and even at 610°C. These low temperatures are also inconsistent with any other measurements on ignition of materials containing Al or nano-Al as fuels. The authors of Granier et al., *Combustion and Flame* 2004; 138(4):373-83 admit that the temperature curves presented are inaccurate and do not account for transient effects and other experimental errors but suggest that such data can be used for qualitative comparison between different size aluminum powders.

**0128** An attempt to obtain a more quantitative characterization of ignition kinetics for nanocomposite reactive materials using laser ignition was made by Hunt et al., *Journal of Applied Physics* 2005; 98:34909-1-034909-8. The nanocomposite system considered was Al—Ni and the material was prepared by ultrasonic mixing of the respective nanopowders. Cylindrical pellets with 55-60% TMD were then pressed and ignited using a CO₂ laser beam. The variation of the measured ignition temperature as a function of the heating rate was obtained. Activation energies were recovered using isoconversion data processing. A dramatic difference in the ignition activation energy for micron-sized and nanosized Al powders was reported. Thermocouple measurements similar to those of Granier et al., *Combustion and Flame* 2004; 138(4):373-83 were used to identify the ignition temperature. Even though the heating rates were rather low, on the order of 1-10 K/min, the error in the thermocouple measurement still needs to be quantified in order for the reported ignition kinetics to be meaningful. Unfortunately, no error analysis for the thermocouple measurements was provided. A summary of activation energies relevant for the Al—Ni reactions, including those occurring in the nanoflakes, is presented by Blobaum et al., *Acta Materialia* 2003; 51:3871-84, which does not include the unusually low activation energy for nanocomposites reported by Hunt et al., *Journal of Applied Physics* 2005; 98:34909-1-034909-8. Generally, a decrease in the particle size is not expected to reduce dramatically the activation energy for any heterogeneous reaction; instead, it is expected to substantially increase the value of the pre-exponential factor in the Arrhenius-type reaction kinetic description. Surprisingly, the values of pre-exponential factors, also determined in Hunt et al., *Journal of Applied Physics* 2005; 98:34909-1-034909-8, are of the same order of magnitude for all micron-sized and nano-sized powders used to prepare composite samples. Finally, the heating rates achieved in Hunt et al., *Journal of Applied Physics* 2005; 98:34909-1-034909-8 are typical for thermal analysis experiments and much higher rates are generally desired in laser ignition configurations.

**0129** Heterogeneous shock tube experiments offer another configuration in which well-defined and high heating rates can be achieved (Bozyn et al., *Combustion Science and Technology* 2007; 179:457-76). In such experiments, a powder-like sample is placed or injected near the wall the “driven” section of a shock tube and the incident and reflected shock waves pass over the sample quickly and heat it in two sequential steps, closely following each other. This way, the sample is nearly instantaneously introduced into a hot gas and its temperature history can be relatively easily calculated with a convective heating model. The sample ignition and combustion are monitored optically and the ignition delay is quantified considering the well-known timing of the reflected shock. This technique is not suitable for the nanocomposite samples prepared as mixed, low density nanopowders because such materials disintegrate after being dispersed by the shock wave. On the other hand, this technique is well suited to study ignition kinetics for nano-sized aluminum powders as well for the fully dense nanocomposite powders prepared by ARM. The results of measurements presented by Bozyn et al., *Combustion Science and Technology* 2007; 179:457-76 are shown in FIG. 21. Ignition delays measured by Bozyn et al., *Combustion Science and Technology* 2007; 179:457-76 for nanosized aluminum powders and nanocomposite thermites were of the order of a microsecond, while millisecond delays were observed for a micron-sized aluminum powder (cf. inset in FIG. 21.) The main combustion peaks in the powder emission were also shifted in time. The most rapid combustion was observed for the Al—MoO₃ nanocomposite thermitite, followed by nearly coinciding peaks for n-Al (ALEX) and Al—Fe₂O₃ nanocomposite thermitite. The combustion peak for the micron-sized Al powder was observed after the longest delay.

**0130** The measurements of ignition kinetics are strongly affected by the particle size distribution in the sample tested and by possible particle agglomeration (especially significant for nanosized powders). Thus, in order to directly validate a quantitative ignition model, detailed characterization of the particle size distribution is necessary and the particle size distribution effect needs to be explicitly addressed in both experimental validations and respective calculations.

**0131** Experimental studies of the ignition of powder-like samples coated on an electrically heated filament were described by Umbrjukar et al., *Propellants, Explosives, Pyrotechnics* 2007; 32(1):32-41; Umbrjukar et al., *Propellants Explosives and Pyrotechnics* 2006; 31(5):382-9; Umbrjukar et al., *Thermochimica Acta* 2006; 451:34-43; Ward et al., *International Journal of Heat and Mass Transfer* 2006; 49(25-26):4943-54; and Shoshin et al., *Combustion and Flame* 2006; 144(4):688-97. The filament temperature was measured in real time using an infrared pyrometer focused on an uncoated filament surface adjacent to the powder coating. The ignition instant was detected optically using a second photo sensor focused on the powder coating. The method provides well-controlled heating rates between 10⁴ and 10⁷ K/s. A detailed analysis of the heat transfer between the filament and the thin layer of the powder coating was presented in Ward et al., *International Journal of Heat and Mass Transfer* 2006; 49(25-26):4943-54 and ignition kinetics for various nanocomposite samples was reported in Umbrjukar et al., *Propellants, Explosives, Pyrotechnics* 2007; 32(1):32-41; Umbrjukar et al., *Propellants Explosives and Pyrotechnics* 2006; 31(5):382-9; Umbrjukar et al., *Thermochimica Acta* 2006; 451:34-43. Ignition temperatures for nanocomposite materials were found to vary in a general range of 600-1000 K (Umbrjukar et al., *Thermochimica Acta* 2006; 451:34-43; Schoenitz et al., *Journal of Propulsion and Power* 2007; 23(4):683-7).

**0132** The kinetics of material ignition determined from experiments performed with different heating rates were compared with the kinetics of various exothermic events observed with the same materials from a thermal analysis (DSC), performed over a different range of heating rates. An example of such comparison for Al—MoO₃ thermites is shown in FIG. 22. The data shown in the coordinates corresponding to the isoconversion processing: the logarithm of...
the ratio of the temperature square over the heating rate \( (T^2/b) \) is plotted against the inverse temperature \( (1/T) \). For clarity, a top axis is added showing the actual temperatures corresponding to the horizontal coordinate. The DSC curve processed is similar to the top curve shown in FIG. 19 and includes a number of exothermic features. Four of the most prominent features were processed from multiple heating rate DSC experiments to obtain a family of lines corresponding to the low heating rate range in FIG. 22. The heated filament ignition experiments, performed at much higher heating rates are shown in the same plot. One immediate conclusion from comparing the filament ignition and DSC inferred kinetic trends is that the strongest peak (represented by open circles and labeled “peak 4” in FIG. 22) observed in the DSC signal at higher temperatures does not really affect ignition of these powders, which occurs at lower temperatures despite much higher heating rates. Thus, the processes occurring at lower temperatures must be responsible for triggering the material ignition. Weaker exothermic events are indeed observed in the DSC curves at lower temperatures (cf. FIG. 19). None of the trends obtained from DSC for the low-temperature events can be directly correlated with the kinetic trend observed for the filament ignition experiments, however. The most likely explanation is that the low-temperature exothermic features observed in the DSC experiments do not represent individual reaction steps but rather are compounded events. The direct extrapolation of kinetic trends for such compounded events observed in the narrow range of heating rates available for DSC measurements to the much higher heating rates (as can be implied by FIG. 22) is poorly justified. Thus, the low-temperature exothermic events need to better characterized in order to predict ignition of such materials. An initial analysis and modeling approach were provided by Umbraljark, et al., Thermochemica Acta 2006; 451:34-43 and Schoenitz, et al. Journal of Propulsion and Power 2007; 23(4):683-7 based on a model of multiple overlapping processes that occur during the sample heating. Isoconversion processing may not be very useful for analysis of such reactions involving steps that overlap and substantially affect one another (Umbraljark, et al., Thermochemica Acta, Submitted, 2008).

Combustion Studies

**Laboratory Tests**


As the initial qualitative features of combustion of nanocomposite materials became established, open tray experiments became more instrumented to obtain more quantitative and meaningful combustion characteristics. Photo diodes with collimated inputs were used to register flame arrival instant and obtain a more accurate measurement of the flame speed (Puszynski, *Proceedings of the 29th International Pyrotechnics Seminar*). Publisher: Defense Science & Technology Organization, Pyrotechnics Group; 2002, p. 191-202; Moore, et al., *Journal of Propulsion and Power* 2007; 23(1): 181-5; Puszynski, *Materials Research Society Symposium—Proceedings* 2003; 800:223-32). Pressure sensors were also used to obtain the pressure signatures of the propagating flames (Sanders, et al., *Journal of Propulsion and Power* 2007; 23(4):707-14). Poor reproducibility between the flame speed measurements in open tray experiments was often observed and it was suggested that the setup could be improved by installing a periodic sequence of baffles with small openings along the channel in which the sample is placed and ignited (Puszynski, *Proceedings of the 29th International Pyrotechnics Seminar*). Publisher: Defense Science & Technology Organization, Pyrotechnics Group; 2002, p. 191-202; Walter, et al., *Journal of Propulsion and Power* 2007; 23(4):645-50). The baffles were meant to minimize the effect of removal or suspension of unignited free powder as a result of the strong convective flows produced by the propagating flames. Improved reproducibility was indeed achieved; however, the measured flame velocities decreased substantially and the mechanism of flame propagation remained unclear.
Further modifications of the experimental methodology have included using cylindrical tubes in which the sample was packed and ignited (Bockman, et al., *Journal of Applied Physics* 2005; 98(6): 1-7 art. no. 064903; Sanders, et al., *Journal of Propulsion and Power* 2007; 23(4):707-14). Such experiments are often referred to as a “confined sample burn.” Usually the tubes are equipped with multiple side openings for pressure transducers and fiber optics cables feeding the flame emission signal to photodiodes for kinetics and emission analyses. As the ends of the tubes are typically open, such confinement of the combustion materials is only partial. Recently, flame propagation in microchannels was reported for nanocomposite thermites (Son, et al., *Journal of Propulsion and Power* 2007; 23(4):715-21) and nano-aluminum-water systems (Ruh, et al., *Journal of the Combustion Institute* 2007; 31 II:2029-36). A sequence of the high speed images illustrating combustion of an Al–MoO₃ thermit prepared by mixing respective nanopowders in a narrow, 2 mm tube (Son, et al., *Journal of Propulsion and Power* 2007; 23(4):715-21). In a related study, electrical conductivity was measured for a burning nanocomposite sample partially confined between two brass electrodes (Tasker, et al., *Journal of Applied Physics* 2006; 99:023705). Electrical contacts were used to measure the flame propagation speed in nanocomposite aluminum-Teflon® materials prepared by mechanical milling (Dolgoborodov, et al., *Khimicheskaya Fizika* 2004; 23(9):85-9; Dolgoborodov, et al., *JETP Letters* 2005; 81(7):311-4; Dolgoborodov, et al., *Khimicheskaya Fizika* 2007; 26(12):40-5) and placed in channels at relatively low densities (typically under 50% TMD). The measured speeds of flame propagation varied in the range of 700-1280 m/s, while independent measurements established that the speed of sound in a similarly prepared sample is only about 100 m/s. Thus, the feasibility of detonation in a nano-scale Al-Teflon mixture was reported. As in the other similar measurements, the measured flame propagation speed was observed to decrease with the increase in mixture density (Dolgoborodov, et al., *Khimicheskaya Fizika* 2007; 26(12):40-5).

Despite a relatively large number of reports, observations based on the apparent flame speed for nanocomposite materials are rather limited. It was reported that the dilution of the nanocomposite materials with inert additives (Prentice, et al., *J. Phys. Chem. B* 2005; 109:20180-5) results in an appreciable reduction of the flame speed. It was also observed that preparing off-stoichiometric compounds can result in an increased flame speed for slightly metal rich cases, e.g., for Al–Cu₃O thermit (Walter, et al., *Journal of Propulsion and Power* 2007; 23(4):645-50) or for Al–MoO₃ thermit (Granier, et al., *Combustion and Flame* 2004; 138(4):373-83; Bockman, et al., *Journal of Applied Physics* 2005; 98(6):1-7 art. no. 064903). On the other hand, it has been reported that an increased flame speed can be maintained when a nanosized aluminum powder is blended with a micron-sized powder. The flame speed for a nanocomposite with the fuel prepared as a blend of micron and nano-sized powders matched that of the nanocomposite prepared with pure aluminum powder when about 60% of nanopowder was added (Moore, et al., *Journal of Propulsion and Power* 2007; 23(1):181-5). As noted above, it was observed that the sample packing density affects the apparent flame speed dramatically; for example a difference by two orders of magnitude was observed for loose and “packed” samples, with respective densities of 5-10% and 35-55% TMD (Sanders, et al., *Journal of Propulsion and Power* 2007; 23(4):707-14). It was also reported in (Sanders, et al., *Journal of Propulsion and Power* 2007; 23(4):707-14) that the effect of packing density on the pressure produced by the burning nanocomposite thermites was opposite to the effect of packing density on the apparent flame propagation velocity.

Interpretations of the apparent flame propagation measurements, often showing supersonic values of the flame speeds for the nanocomposite materials, are difficult. The convective flow patterns are better defined for the partially confined samples, but the thermal properties of the loosely packed or even pressed nanocomposite samples critical for description of the flame propagation remain poorly quantified. These properties are likely changing dramatically as the propagating flame heats up the sample and/or as the sample is compressed by the pressure wave generated by the flame front. The magnitude of such changes is likely comparable to that observed for the electrical properties of the nanocomposite mixtures affected by the flame propagation (Tasker, et al., *Journal of Applied Physics* 2006; 99:023705). Simplified heat transfer models for flame propagation in confined and unconfined nanocomposite materials are offered in refs. (Walter, et al., *Journal of Propulsion and Power* 2007; 23(4):645-50; Wilson, et al., *AIAA Paper* 2003-4536, 2003; Wilson, et al., *AIAA Paper* 2005-0275, 2005). These models operate with lumped time scales and bulk burn rates and do not include the inherent reaction kinetics and varied transport properties of the reacting materials. Such models are attractive for practical users but the multiple simplifying assumptions made are not currently justified. It is possible to select the adjustable parameters to fit a selected experimental data set, it is unreasonable to expect that the same parameters will be useful in predicting combustion behavior for materials with altered properties or burning in a different configuration.

Changes in the thermodynamic and transport properties of the reacting materials need to be considered. For example, an enhanced heat transfer is expected when gasified reduced metal formed in a thermit reaction, such as Mo (or Cu and Bi) condenses on unignited or burning particles (Son, et al., *Journal of Propulsion and Power* 2007; 23(4):715-21). In another recent report, it was suggested (Sanders, et al., *Journal of Propulsion and Power* 2007; 23(4):707-14) that the flame propagation mechanism can be compared to convective detonation (Ershov, *Fizika Goreniya i Vzryva* 1997; 33(1):98-106; Ershov, et al., *Fizika Goreniya i Vzryva* 2001; 37(2):94-102) for flame propagation in a porous medium with a thin surface layer of explosive.


Because combustion may not follow the equilibrium thermodynamic predictions, thermodynamic calculations can only serve as an initial guideline for interpreting the experimental results. Despite such difficulties, it appears that comparison of different materials, or materials prepared from the same compounds but with different particle sizes or morphologies, can be very meaningful based on such pressure measurements. Both maximum pressures achieved and the rates of pressure rise are of interest. In addition, the final pressure in the chamber after the reaction is completed and the products are cooled, is of interest as indicative of the final make-up of the gaseous reaction products. Finally, condensed reaction products can be readily recovered and analyzed, yielding information important for development of the reaction mechanism. Sets of related measurements with reactive nanocomposite materials prepared by ARM are presented by Umbrajkar, et al., *Journal of Propulsion and Power* 2008; 24(2):192-8 and Truov, et al., *Journal of Propulsion and Power* 2008; 24(2):184-91. Because these materials comprise fully dense micron-sized particles that retain their morphology and structure upon being dispersed in a gaseous oxidizer, the composites ignited and burned uniformly when aerosolized in the explosion vessel (Umbrajkar, et al., *Journal of Propulsion and Power* 2008; 24(2):192-8; Truov, et al., *Journal of Propulsion and Power* 2008; 24(2):184-91). Thus, the pressure measurements were interpreted in terms of the flame propagation speed, in addition to the straightforward interpretation of the maximum achieved pressure as an indicator of the overall energy release.

Details available in the literature are insufficient for meaningful comparison of different pressure measurements or other experimental data for this type of experiments reported by different research groups. It is suggested that future experiments in confined vessel experiments specify the cell volume, mass of the powder load, and the initial and final pressures obtained. Furthermore, the type of gas present in the pressure cell and the pressure increase obtained from the igniter itself (without the nanocomposite powder) would be useful for meaningful comparisons of the data from different investigators.

Measurements describing combustion of individual reactive nanocomposite particles prepared by ARM were recently reported (Beloni, et al., *AIAA Paper* 2007-1431, 2007). The powder-like material was incorporated into a liquid fuel (decane) and the produced slurry was aerosolized using an ultrasonic nozzle. The aerosol jet was burned in a lifted laminar flame configuration and the combustion of nanocomposite particles was studied optically. It was observed that micron-sized aluminum particles could not be ignited in this configuration; however, the same or coarser size nanocomposite reactive particles with bulk composition 28+42 ignited and burned completely. The ignited particles were also observed to disintegrate during their combustion and continue burning as smaller fragments. This type of combustion is very attractive for practical applications where rapid burn rates are desired for particles that are coarser and easier to work with than nanopowders.

Heterogeneous shock tube measurements were mentioned earlier as useful for finding ignition delays (Bazyn, et al., *Combustion Science and Technology* 2007; 179: 457-76). The same measurements are also useful for characterization of the ensuing combustion of the aerosolized material. If the material can survive the initial interaction with the incident and reflected shock waves without being disintegrated, the information obtained from detailed optical measurements can be used to determine the burn rates, combustion temperatures, and identify some of the product species formed, all of which is critically important for developing meaningful combustion models. The issues of the material survival are effectively removed when combustion of n-Al in gaseous oxidizers is studied (Bazyn, et al., *Combustion and Flame* 2006; 145(4):703-13) using the heterogeneous shock tube technique. The results are very interesting and show substantial differences between combustion of n-Al and relatively well characterized combustion of micron-sized Al particles. It was found that the burn time of n-Al particles decreases rapidly with the increase in the ambient gas temperature. Furthermore, substantial reduction of the combustion time was also observed for n-Al at increased pressures. These combustion features are indicative of a kinetic burning regime for n-Al.

Comparison of combustion features of micron- and nanosize Al powders was also presented by Huang, et al., *Proceedings of the Combustion Institute* 2007; 31(1):2001-9. Experiments employed a premixed Bunsen-type flame with Al-laden flow fed from the burner's nozzle. Bimodal nano- and micron sized Al particles were used to produce laminar flames for which the speed and optical structure were studied and interpreted theoretically.


Performance in Practical Applications

Development of new reactive nanomaterials is driven by their potential applications in propellants, explosives, and pyrotechnics. Experimental validations of the performance of related practical formulations are, therefore, very important for justifying further research and for guiding the material development efforts. Because reactive nanomaterials became available only recently, the published results describing their performance are relatively scarce. Some of the first demonstrations of the effect of replacing micron-

**Example 1**

A SPEX 8000 shaker mill has been used extensively in current research on reactive milling and mechanical alloying [Suryanarayana, Progress in Materials Science, 46 (2001) 1-184; Shoshin, et al., Combust. Flame 128 (2002) 259-269; Schonemitz, et al., J. of Prop. and Power 19(3) (2003) 405-412] and was also used in this and the other Examples. The SPEX shaker mill is a vibratory mill; its vial is agitated at high frequency in a complex cycle that involves motion in three orthogonal directions. The reciprocating velocity of the vial in the SPEX 8000 series shaker mill is directly proportional to the motor’s rotational speed. Under various loading conditions, the rotational speed of the actuator input shaft was measured with a stroboscope. The nominal rotational speed was 1054 RPM, which translates to an oscillation frequency of 17.6 Hz. The vial speed was not varied in the present Examples, but it offers additional means of control over the milling process as the vial speed directly influences the impact velocity and frequency of collisions, and hence the energy transferred to the powder from the plastic deformation. Steel milling vials and balls were used in this and the remaining Examples. Milling media with higher or lower densities can also be used to afford control over the collision energy between the media.

**Example 1**

A thermistor was mounted on the milling vial and connected to a PC-based data logger to monitor its temperature. The spontaneous reaction occurred as a sharp temperature spike. Times of initiation were determined for varying milling parameters for each material. No process control agent was used. The diameters of the balls used were 2.36, 3.16, 4.76, and 9.52 mm. The materials were milled under argon. The ball-to-powder weight ratio (charge ratio, C_p) was set to 2.5, 5, and 10.

**Example 2**

Starting materials were Al (98%, 10-14 μm), Fe_2O_3 (99.5%, ~325 mesh), and MoO_3 (99.5%, ~325 mesh) from Alfa Aesar. The total amount of material was 5 g in the case of Al—Fe_2O_3, and 2 g for Al—MoO_3. At a given C_p, this changes the number of balls used, and therefore the milling times required to initiate the spontaneous reaction for different materials are not immediately comparable. The amount of the Al—MoO_3 mixture loaded in a single run did not exceed 2 g to avoid damaging the milling vial because of the high local temperatures caused by the reaction.

**Example 3**

After initiation times were determined, samples of metastable composite materials were prepared using Arrested Reactive Milling (ARM) by halting the milling just before the initiation of the reaction. Stoichiometric Samples of Al—Fe_2O_3 and Al—MoO_3 were prepared with varying milling times. The respective reproducibility of the initiation under identical milling conditions was found to be about 10% (see below). Therefore, samples arrested at approximately 90% of the time of spontaneous initiation are designated as “fully milled” for reference. Partially milled samples were obtained at approximately 50% initiation time.

**Materials Characterization**

Powder x-ray diffraction was performed using a Philips X’pert MRD X-ray diffractometer. The surface morphology of individual particles was as well as the internal structure of cross-sectional particles was investigated using a LEI 1530 Field Emission Scanning Electron Microscope (SEM). Cross sections were prepared by embedding small quantities of composite powders in epoxy resin. The particles

**Description of the Preferred Embodiments**

The invention is further illustrated in the following Examples, which however are to be considered as exemplary and not definitive of the invention.
were embedded under vacuum to eliminate trapped gasses and avoid formation of bubbles. The mounts were then polished by hand using successively finer SiC polishing paper up to 1200 grit.

Example 2
Combustion Testing

Several preliminary tests were carried out to assess changes in the ignition and combustion behavior of the Nano-composite thermite materials produced by ARM. Schematic diagrams of the experimental setups are shown in FIG. 1.

Ignition of the ARM-prepared powders was studied using an electrically heated filament (FIG. 1a). This technique has been described extensively elsewhere (Trunov, et al., *Chemical and Physical Processes in Combustion*). The 2003 Technical Meeting of the Eastern States Section of the Combustion Institute University Park, Pa. (2003) pp. 313-316; Mohan, et al., *Chemical and Physical Processes in Combustion*. The 2003 Technical Meeting of the Eastern States Section of the Combustion Institute University Park, Pa. (2003) pp. 329-332. A thin layer of powder is coated on a conductive filament, which is electrically heated at varying rates. Ignition of the powder is registered using a photodiode focused on the powder coating. The temperature of the filament is measured simultaneously with an infrared pyrometer focused on an uncoated area of the filament adjacent to the powder. This setup minimizes errors due to unknown emissivities of different powders. From the ignition temperatures measured in this setup at different heating rates, the activation energy can be estimated by treatment analogous to isoconversion methods used in conventional thermal analysis (Starink, *Thermochemical Acta* 288 (1996) 97-104).

In another test, reaction rates were compared for nano-composite powders prepared using ARM and blended initial component powders. In these tests, the thermite powder was placed on a ceramic support inside a closed pressure vessel equipped with a pressure transducer (FIG. 1b). Prior to the experiment, the vessel was purged with argon. The powder charge was ignited using a heated wire. The powder was not dispersed prior to ignition. However, most of the powder was airborne during the combustion due to the expansion of surrounding and pore gas as well as due to the production of intermediate volatile products. Pressure traces were recorded, and combustion products were collected for x-ray phase analysis.

Linear burning rates of different powders were measured in the test illustrated in FIG. 1c. The powders were placed in an open, rectangular groove of 2.5 times 2.5 mm cross-section cut into a block of ceramic. Samples were initiated on one end with an electrically heated wire. The propagation of the combustion front was recorded with a high-speed video camera at 500 frames per second.

Observed times of spontaneous ignition during milling of Al—MoO₃ and Al—Fe₂O₃ are shown in Table 1. The values and errors shown are the results of 2-4 repetitions under identical conditions. The reproducibility is found to be on the order of ±10%. Milling times generally decrease with increasing charge ratio Cᵅ.

<p>| TABLE 1 | Milling times (minutes) required for spontaneous initiation of stoichiometric mixtures of Al—MoO₃ and Al—Fe₂O₃ for specific ball sizes and charge ratios. |</p>
<table>
<thead>
<tr>
<th>Ball size, mm</th>
<th>Cᵅ = 2.5</th>
<th>Cᵅ = 5</th>
<th>Cᵅ = 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al—MoO₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.36</td>
<td>39.2 ± 1.1</td>
<td>33.2 ± 1.8</td>
<td>7.75 ± 0.21</td>
</tr>
<tr>
<td>3.16</td>
<td>24.2 ± 2.4</td>
<td>13.9 ± 0.1</td>
<td>7.05 ± 0.07</td>
</tr>
<tr>
<td>4.76</td>
<td>22.8 ± 0.8</td>
<td>11.4 ± 0.6</td>
<td>5.85 ± 0.07</td>
</tr>
<tr>
<td>9.52</td>
<td>35.4 ± 6.4</td>
<td>9.65 ± 0.9</td>
<td>4.60 ± 0.14</td>
</tr>
<tr>
<td>Al—Fe₂O₃</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.36</td>
<td>169 ± 0.4</td>
<td>14.8 ± 1.1</td>
<td>8.93 ± 0.64</td>
</tr>
<tr>
<td>3.16</td>
<td>59.0 ± 7.1</td>
<td>18.1 ± 0.5</td>
<td>9.47 ± 0.39</td>
</tr>
<tr>
<td>4.76</td>
<td>41.6 ± 4.1</td>
<td>20.5 ± 3.6</td>
<td>10.0 ± 1.03</td>
</tr>
<tr>
<td>9.52</td>
<td>33.6 ± 4.3</td>
<td>11.7 ± 4.3</td>
<td>9.42 ± 0.74</td>
</tr>
</tbody>
</table>

Recently, it has been suggested that the progress of mechanical alloying or reactive milling can be described using the specific milling dose, Dₘ, introduced as

\[ Dₘ = \frac{n_{coll} E_{coll}}{m_p} \]

where \( I \) is the milling intensity, \( n_{coll} \) is the frequency of ball-ball collisions, \( E_{coll} \) the averaged energy per collision, \( t \) the milling time, and \( m_p \) the powder mass. It was assumed that the value of \( Dₘ \) determines the state of the milled material, and that ignition is triggered at a specific degree of grain refinement. Further simplifying assumptions can be made, i.e., \( E_{coll} \approx m_p \), where \( n \) is the number of balls. With the time of the initiation, \( t_{init} \), this leads to a constant milling dose, \( Dₘ \), corresponding to a certain degree of grain refinement:

\[ Dₘ = \frac{n_{coll} E_{coll}}{m_p} = \frac{Cᵅ m_p}{C_p m_p} \]

The definition for the charge ratio \( C_p = n/m_p \) was used. Thus, for a certain degree of refinement, it is expected that \( C_p \) remains constant.

This reasoning suggests that the milling time required to trigger initiation depends on the diameter of the milling balls exclusively vs. the charge ratio. A similar relation was suggested earlier (Delogu, et al., *Chemical Engineering Science* 58 (2003) 815-821). However, the analysis of mechanical alloying processes presented in (Delogu, et al., *Chemical Engineering Science* 58 (2003) 815-821) was based on a kinetic expression for very low degrees of milling-induced amorphization, and led to the conclusion that for a given milling state \( C_p \), the ball diameter should be constant.

The product of the measured milling times leading to initiation and the charge ratios, \( C_p t_{init} \), is plotted as a function of the ball diameter in FIG. 2. The values of \( C_p t_{init} \) for series with different \( C_p \) superimpose and do not change significantly. Thus, to first approximation, the present observations appear to support the tentative trend as expected from Eq. (3), rather than constant values of \( C_p t_{init} \).
different length scales for initiation to occur, the observed dependence on the ball diameter is not intuitive. Both the achieved degree of structural and compositional refinement and the collision energy determined by the ball diameter could be important for initiation.

Example 3

[0164] Based on the good reproducibility of the experiments with balls of 4.76 mm diameter, reactive composites were prepared for further analysis with these balls and with C_p = 5. “Fully milled” materials were milled for 11 and 19 min for the Al—MoO_3 and Al—Fe_2O_3 mixtures, respectively. “Partially milled” materials were milled for about half the maximum time, 6 and 10 min, respectively. In addition, fully reactive B—Ti nano-composite powders were prepared by milling elemental B and Ti powders in steel vials for 150 min using steel balls with diameters of 4.76 mm and a C_p of 5. Thermite powder blends were prepared by manually homogenizing the starting materials under acetone for reference tests.

Materials Properties

[0165] SEM images of the fully milled nano-composite particles and particle cross-sections are shown in FIG. 3. The particles’ surface morphology is typical for mechanically alloyed powders. The images of the particle cross-sections show that the initially spherical Al is thinned out to layers of 10-100 nm thickness sandwiched between layers (MoO_3) or nanosized particles (Fe_2O_3) of oxidizer. XRD showed no structural changes in either Al or the respective oxides, although noticeable peak broadening was observed for all materials indicating a reduction in crystallite sizes. Particle size distributions measured using LALLS are shown in FIG. 4. While the shape of the distribution changes, the average particle size of the reactive composite is close to the size of the starting materials. The size reduction implied by the LALLS data for partially milled Al—MoO_3 is not supported by direct inspection of the particles by microscopy. However, the partially milled particles are oblate, therefore, the light scattering-based measurement is likely to produce erroneous results. The shapes of the fully milled/reactive particles are sufficiently close to spherical to justify the use of LALLS.

Example 4

Preliminary Ignition and Combustion Testing

[0166] Ignition temperatures measured at different heating rates for the three types of fully reactive nano-composite materials prepared using ARM are shown in Table 2. These data, processed using an isocconversion method (Starink, Thermo-chemica Acta 288 (1996) 97-104) to estimate the ignition activation energy, are plotted in FIG. 5. For comparison, similarly measured and processed experimental data describing ignition of pure Al and Mg powders in air (Trunov, et al., Chemical and Physical Processes in Combustion. The 2003 Technical Meeting of the Eastern States Section of the Combustion Institute University Park, Pa., (2003) pp. 313-316; Mohan, et al. Chemical and Physical Processes in Combustion. The 2003 Technical Meeting of the Eastern States Section of the Combustion Institute University Park, Pa., (2003) pp. 329-332) are also shown in FIG. 5. The activation energies for ignition of pure Al and Mg powders in air are close to 215 kJ/mol and are noticeably higher than those measured for the thermites and B—Ti nano-composites. The evaluated activation energies for the Al—Fe_2O_3 and Al—MoO_3 nano-composites are 170.4±0.25 kJ/mol and 152.4±0.19 kJ/mol, respectively, and are close to each other. These values are close to the activation energy of 167.5 kJ/mol reported for the Al—Fe_2O_3 thermite reaction in (Maximov, et al., Zhurnal Fizicheskoi Khimii 40(2) (1966) 467-470 (in Russian)). The activation energy for ignition of the B—Ti nano-composites is significantly lower, 59.4±0.15 kJ/mol. In general, the activation energies are expected to be unaffected by the nano-composite mixing of the ingredients using ARM. However, the activation energies of the thermite compositions prepared by mixing passivated nano-powders could be somewhat higher due to the passivating (e.g., oxide) layers.

<table>
<thead>
<tr>
<th>Heating Rate, K/s</th>
<th>Ignition Temperature, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>3096</td>
<td>1104</td>
</tr>
<tr>
<td>972</td>
<td>1027</td>
</tr>
<tr>
<td>340</td>
<td>995</td>
</tr>
<tr>
<td>3438</td>
<td>1249</td>
</tr>
<tr>
<td>883</td>
<td>1207</td>
</tr>
<tr>
<td>291</td>
<td>1110</td>
</tr>
<tr>
<td>B_62Ti_38</td>
<td></td>
</tr>
<tr>
<td>412</td>
<td>600</td>
</tr>
<tr>
<td>1335</td>
<td>678</td>
</tr>
<tr>
<td>5732</td>
<td>732</td>
</tr>
</tbody>
</table>

Example 5

[0167] Pressure traces measured in the constant volume explosion vessel for combustion of different charges of thermite powders are shown in FIG. 6. While only qualitative conclusions can be drawn from the comparisons of the pressure traces measured for different powders, samples were portioned to provide a constant 17.9 kJ of energy (4.50 g for Al—Fe_2O_3, and 3.81 g for Al—MoO_3 compositions). Powder blends, fully and partially reactive nano-composite powders prepared using ARM with different milling times were used in these tests. A summary of the measured pressures and rates of pressure rise for different samples is given in Table 3. A clear trend of the accelerated reaction rate for ARM-prepared materials is visible from the comparison of the pressure traces shown in FIG. 6 and from the results shown in Table 3. It is also seen that the highest reaction rates are observed for fully milled powders of both, Al—Fe_2O_3 and Al—MoO_3 thermites. Finally, a higher reactivity for the Al—MoO_3 thermites compared to the Al—Fe_2O_3 thermites is generally observed.
The combustion products collected from the pressure vessel were analyzed by SEM and XRD. A representative backscattered electron image is shown in FIG. 7. Product particles consist of aluminum oxide with caps of the respective reduced metal. This feature appears to be independent of particle size, as it is even observed in 10 nm particles in the airborne fraction. XRD showed that the bulk of aluminum oxide found in the Mo products was \( \gamma \)-\( Al_2O_3 \), while it was \( \alpha \)-\( Al_2O_3 \) in the Fe products. Small amounts of \( \alpha \)-\( Al_2O_3 \) were found in both cases as well. Increasing amounts of unreacted Al and Fe\(_2O_3\) were detected in the products of partially milled and unalumined Al–Fe\(_2O_3\) composites.

The same pressure vessel has recently been used for constant volume aerosol explosion tests carried out in air with different mechanically alloyed powders (Schoenitz, et al., J. of Prop. and Power 19(3) (2003) 405–412). Nano-composites prepared using boron and titanium powders using ARM were made and compared with the respective powder blends. Higher rates of pressure rise were reported for the nano-composite powders and a higher degree of conversion of the metallic powders to oxides was observed. Interestingly, some borides (e.g., \( TiB \) or \( Ti_3B \) ) were detected in the combustion products of \( Ti \) powder blends but no borides were found in the combustion products of the ARM-prepared \( Ti \) nano-composite powders. More details on these experiments are available elsewhere (Schoenitz, et al., op. cit.).

The results of the linear burn measurements for Al–Fe\(_2O_3\) nano-composites prepared using ARM with different milling times as well as for the blended Al and Fe\(_2O_3\) powders are shown in FIG. 8. The powder blend was successfully ignited, but combustion did not propagate. The propagation was generally faster and the flame speed was more uniform for the powder for which the milling was halted just prior to the expected spontaneous reaction. These results generally confirm that faster reaction kinetics is achieved for materials prepared by ARM.

The foregoing demonstrates that the reactive milling of powders with very high reaction enthalpies can be reproducibly arrested to produce novel energetic material powders with particles in the 1-100 \( \mu m \) size range. Individual particles of these powders are fully dense. The composition of each particle is identical to the bulk powder composition. The components are intimately mixed in three-dimensional nano-structures and ready to react upon initiation. An experimental parametric study of the arrested reactive milling established that for a range of sizes of the grinding balls used, a concept of a milling dose proportional to the product of the milling time and charge ratio can be used to approximately predict the time necessary to prepare the metastable nano-composites. Ignition temperatures of the prepared materials were measured and their activation energies of ignition were evaluated. The activation energy obtained from these experiments for the Al–Fe\(_2O_3\) nanocomposite is consistent with the known activation energy of the Al–Fe\(_2O_3\) thermite reaction. Higher reaction rates were observed in combustion tests conducted in a constant volume pressure vessel in argon for the ARM-prepared nano-composites of both Al–Fe\(_2O_3\) and Al–Mo\(_2O_3\) as compared to the respective blends of initial powders and partially milled powders. Linear burning rates were observed to increase for the ARM-prepared powders as the time when the reactive milling was arrested approached the expected time of the spontaneous reaction in the milling vial.

While the present invention has been described in terms of specific embodiments thereof, it will be understood in view of the present disclosure, that numerous variations upon the invention are now enabled to those skilled in the art, which variations yet reside within the scope of the present teaching. Accordingly, the invention is to be broadly construed, and limited only by the scope and spirit of the claims now appended hereto.

We claim:

1. A metastable nano-composite material produced by a method consisting essentially of:
   (a) reactively milling a mixture of powdered components that spontaneously react at a known duration of said milling;
   (b) stopping said milling at a time at which said components are compositionally homogenized on a nanoscale to produce a nanocomposite powder but prior to said known duration, and thereby before said spontaneous reaction occurs;
   (c) recovering as a product the milled powder as a nanostructured composite for subsequent use by controllably initiating destabilization thereof.

2. A metastable nano-composite material in accordance with claim 1 comprising particles in the 1-50 \( \mu m \) range.

3. A metastable nano-composite material in accordance with claim 1 that is highly reactive.

4. A metastable nano-composite material in accordance with claim 1 that is compositionally homogenized.

5. A metastable nano-composite material produced by a method consisting essentially of:
   (a) selecting starting components as two or more powdered materials capable of a highly exothermic reaction;
   (b) reactively milling said starting components to achieve homogeneity;
   (c) stopping said milling at a time at which said components are compositionally homogenized on the nanoscale to produce a nanocomposite powder, but prior to initiation of said exothermic reaction;
   (d) recovering as a product the milled powder as a metastable nano-composite for subsequent use by controllably initiating destabilization thereof.

6. A metastable nano-composite material in accordance with claim 5 comprising particles in the 1-50 \( \mu m \) range.
7. A metastable nano-composite material in accordance with claim 5 that is highly reactive.

8. A metastable nano-composite material in accordance with claim 1 that is compositionally homogenized.

9. A metastable nano-composite material substantially in powder form.

10. A metastable nano-composite material according to claim 9 that undergoes an exothermic reaction more quickly or at a lower temperature than materials previously available.

11. A metastable nano-composite material according to claim 9 that undergoes an exothermic reaction in at least about 10% shorter time than the time required for materials previously available to undergo a similar or the same reaction at a given heat flow.

12. A metastable nano-composite material according to claim 9 that begins to react in an exothermic reaction at a temperature that is at least about 10% lower than the temperature at which materials previously available begin to react in the same or a similar reaction at a given heat flow.

13. A metastable nano-composite material according to claim 9 that begins to react in an exothermic reaction at a temperature that is at least about 50 or more degrees Kelvin lower than the temperature at which materials previously available begin to react in the same or a similar reaction at a given heat flow.

14. A metastable nano-composite material according to claim 9 that begins to react in an exothermic reaction at a temperature that is at least about 100 or more degrees Kelvin lower than the temperature at which materials previously available begin to react in the same or a similar reaction at a given heat flow.

15. A metastable nano-composite material according to claim 9 wherein most or all particles are between 1-100 microns in diameter.

16. A metastable nano-composite material according to claim 9 wherein at least about half of particles are smaller than about 50 microns in diameter.

17. A metastable nano-composite material according to claim 9 wherein at least about half of particles are smaller than about 30 microns in diameter.

18. A metastable nano-composite material according to claim 9 wherein most or all inclusions in the material are about 50-200 nanometers in diameter.

19. A metastable nano-composite material according to claim 9 that is 25% or more denser than similar materials of the same elements produced by other means.

20. A metastable nano-composite material according to claim 9 that substantially completes an ignition reaction in at least 10% less time than the time required for similar materials of the same elements produced by other means at a given heating rate to substantially complete an ignition reaction.

21. A metastable nano-composite material according to claim 9 that substantially completes an ignition reaction in at least 25% less time than the time required for similar materials of the same elements produced by other means at a given heating rate to substantially complete an ignition reaction.

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