



US 20060090593A1

(19) **United States**

(12) **Patent Application Publication**
Liu

(10) **Pub. No.: US 2006/0090593 A1**

(43) **Pub. Date: May 4, 2006**

(54) **COLD SPRAY FORMATION OF THIN
METAL COATINGS**

(52) **U.S. Cl. 75/252; 427/199**

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(57) **ABSTRACT**

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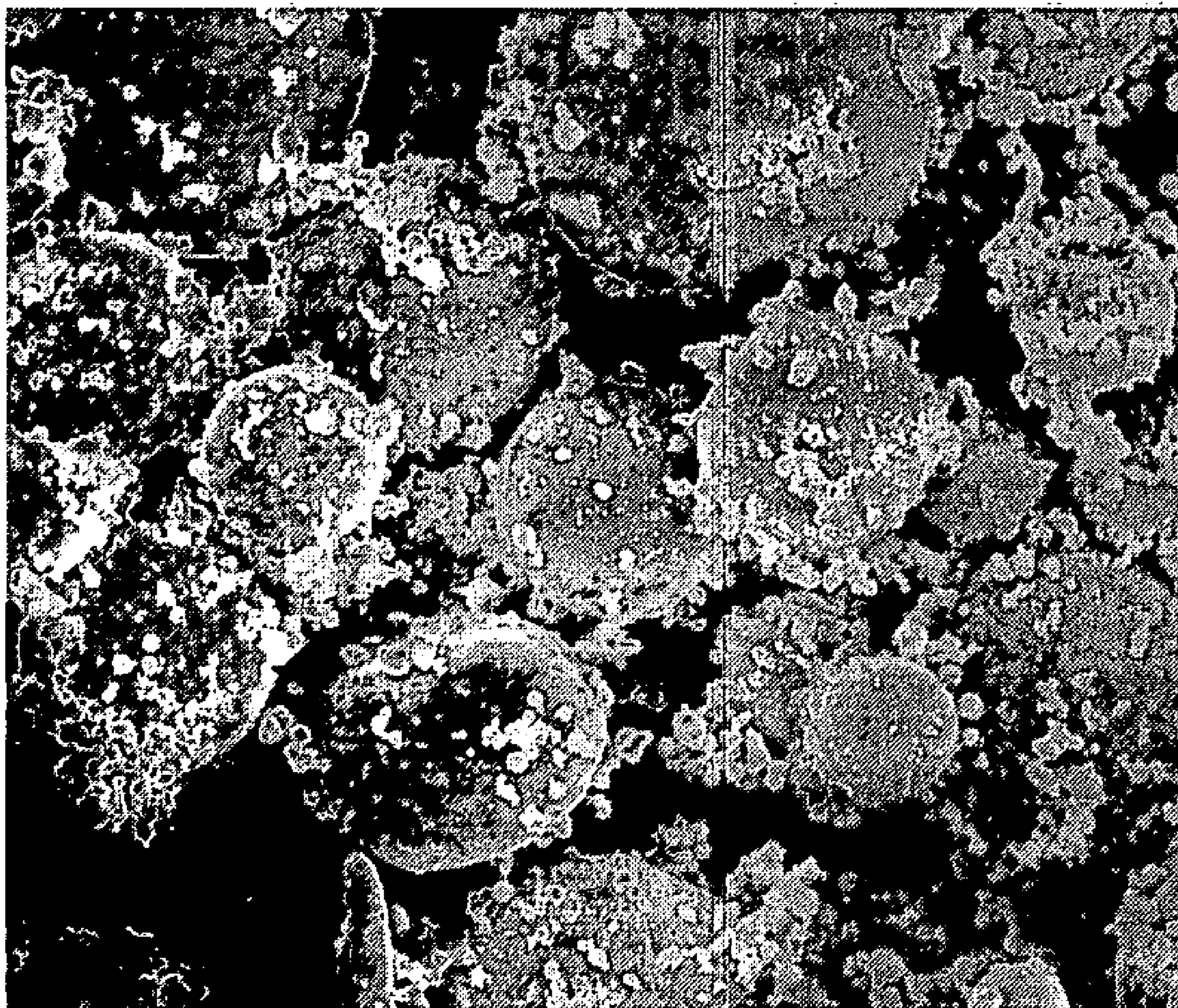
(21) **Appl. No.: 10/980,708**

(22) **Filed: Nov. 3, 2004**

Publication Classification

(51) **Int. Cl.**
C22C 1/05 (2006.01)

The invention relates to an adaptation of the cold spray process to provide a method of coating fine metal particles, including aluminum and copper, onto a work piece. In one embodiment, the invention is a metal agglomerated hard sphere composition capable of providing about a 1 micron or thicker coating of a metal on a work piece in a cold spray process. In another embodiment the invention is a method of coating metal particles, including metal particles having a particle size of about 0.01 to about 10 micron, onto a work piece. The method of the invention circumvents many of the problems associated with cold spray processing of very fine particles.



70µm

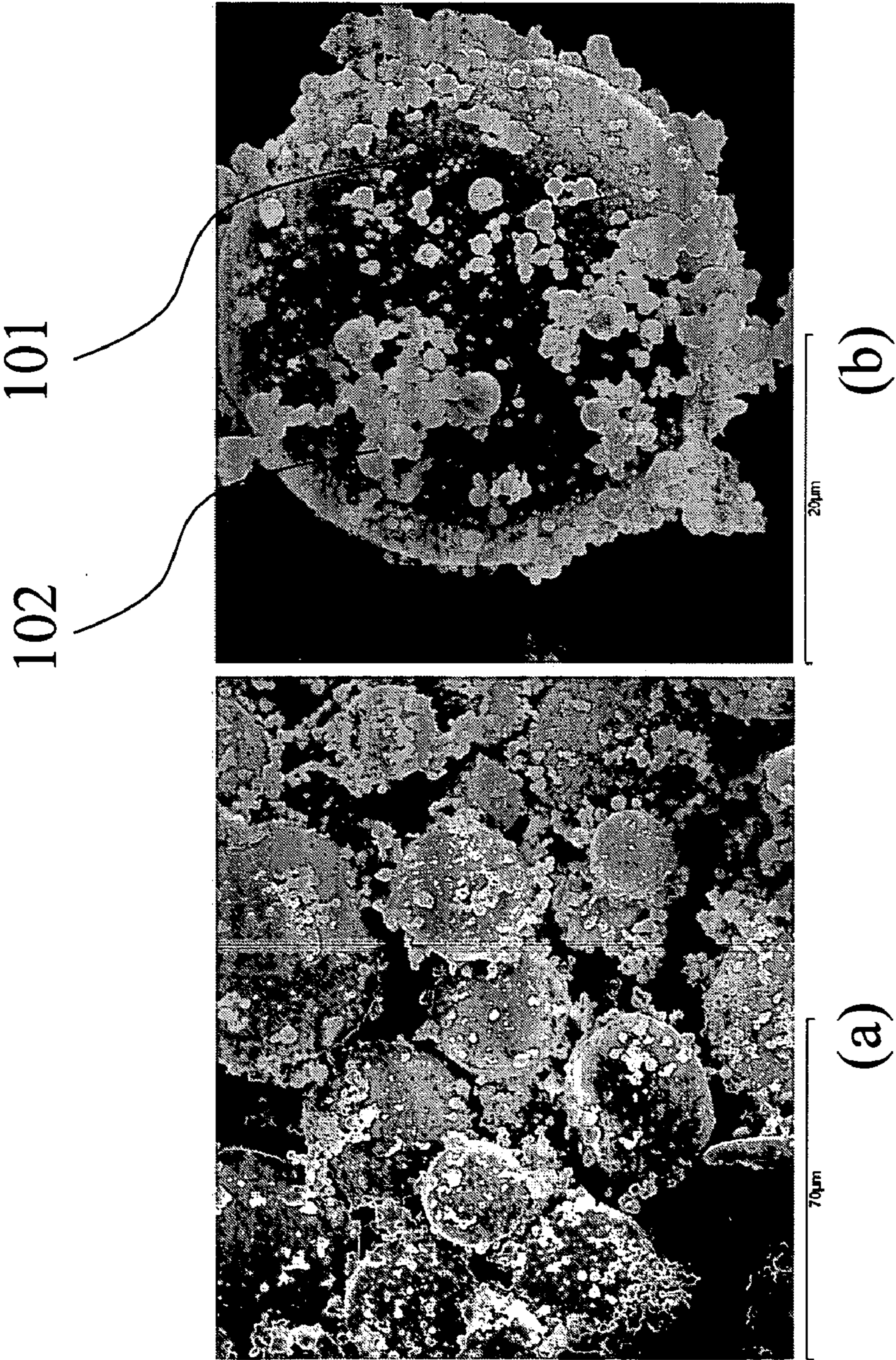


FIG. 1

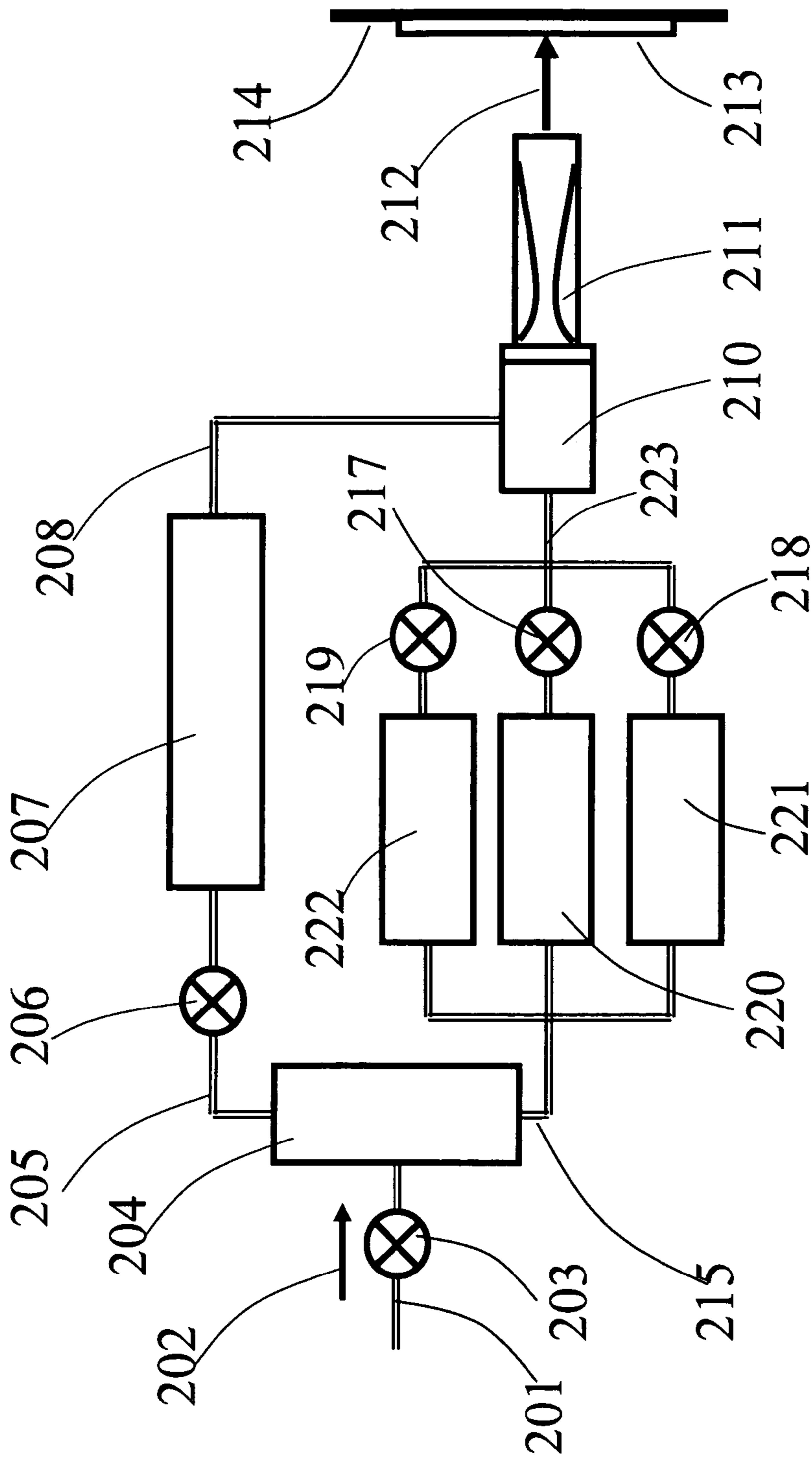


FIG. 2

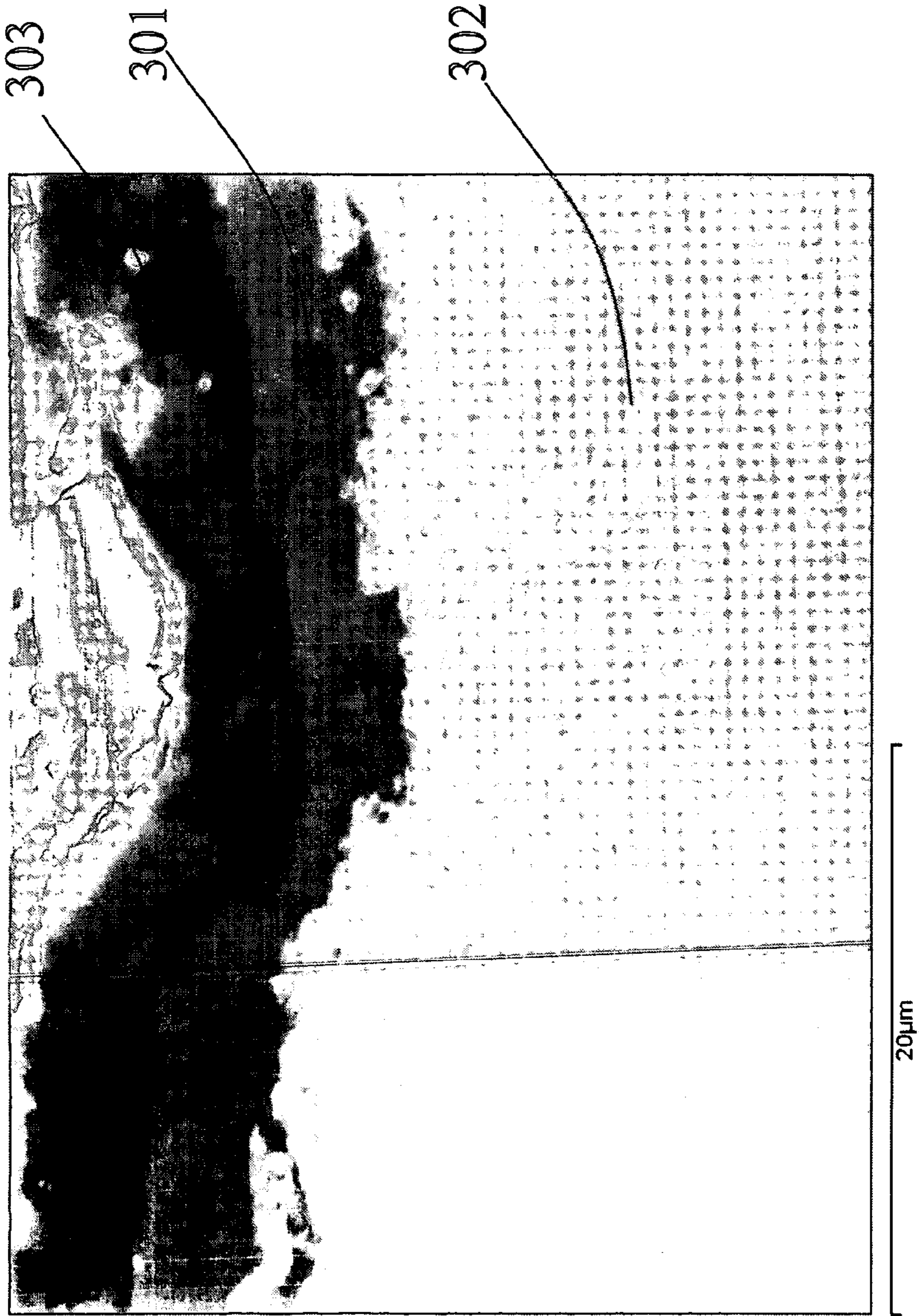


FIG. 3

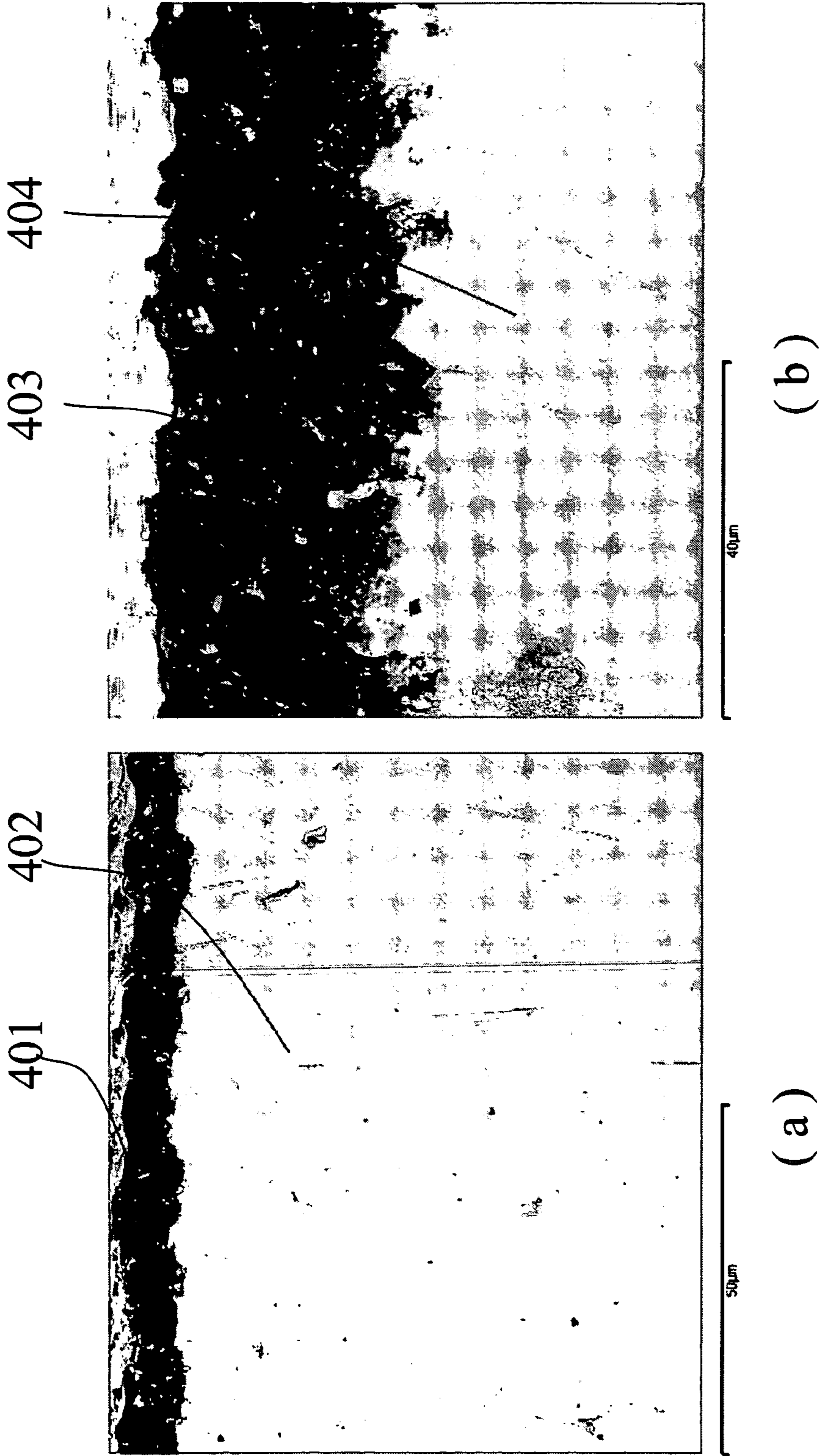


FIG. 4

COLD SPRAY FORMATION OF THIN METAL COATINGS

[0001] This invention was made with United States Government support under Agreement No. N00421-04-P-0625 awarded by Navy Air System Command. The United States Government has certain rights in the invention.

BACKGROUND OF INVENTION

[0002] 1. Field of Invention

[0003] The present invention relates to metallurgy and more specifically to cold spray processing of metal powders to form thin metal coatings onto a work piece.

[0004] 2. Description of Related Art

[0005] U.S. Pat. No. 5,302,414 dated Apr. 12, 1994, incorporated herein by reference, and related re-examination certificate U.S. Pat. No. B1 5,302,414 dated Feb. 25, 1997, describe a cold gas dynamic spraying method for applying a coating, also referred to as cold spraying. That patent describes a process and apparatus for accelerating solid particles having a size from about 1-50 μm to supersonic speeds in the range of 300-1,200 m/sec and directing the particles against a substrate surface. When the particles strike the substrate surface, the kinetic energy of the particles is transformed into plastic deformation of the particles, and a bond is formed between the particles and the target surface. This process forms a dense coating with little or no thermal effect on the underlying substrate surface. The cold spray processing allows formation of dense, low-oxide-content deposits of a wide range of metals and other ductile materials, on a variety of substrates, in air and at near-ambient temperatures.

[0006] There are significant advantages to the cold spray process concept especially for repair of damaged surfaces. Because the process occurs essentially at room temperature, many reactive metals such as aluminum and copper can be used in an open-air environment with little or no oxidation. Also, nearby undamaged surface is not exposed to extreme temperature or chemical conditions used in conventional repair processes. Because the work piece is at ambient pressure, that is, no vacuum chamber is required; they often can be repaired in field places. U.S. Pat. No. 6,491,208, for instance, describes a cold spray repair process, wherein the cold spray process is used in lieu of welding or brazing to repair a superalloy turbine blade. U.S. Pat. No. 6,258,402 describes a cold spray process for repairing spray-formed tooling comprising cold-spraying an initial layer of low-carbon steel.

[0007] By using cold spray, the deposition rate can be as high as 50 grams per minute or more depending on the nozzle size and spray gas flow rate. Also, the deposition rate can be as low as one or two grams per minute or less if a thin coating is required. Many gases can be used for this purpose including compressed air, argon, helium, carbon dioxide, and nitrogen. Many metals and alloys can be used for coating materials including aluminum, copper, zinc, iron, vanadium, cobalt, nickel, lead, WC—Co alloy, stainless steel, aluminum-zinc alloy, copper-zinc alloy, and nickel-zinc alloy. A mixture of the metals or alloys (ductile) with ceramics (non-ductile) also has been used for cold spray coating. For instance, U.S. patent application publication 2004/0202885, Seth, et al, describe the formation of a

composite coating wherein a carbide ceramic is intermixed with particles of a metal matrix.

[0008] In cold spray processing, if a particle has an impact velocity greater than some critical velocity (V_c), it can adhere to the substrate. The critical velocity is a function of several factors including mass of the particle, ductility of the particle, hardness of the substrate, temperature of spray gas. Essentially the kinetic energy must be sufficient to make the particle and the substrate surface deform plastically so that a good adhesion coating can be formed. Usually particles with large mass and ductility have a relatively low V_c to form a coating with good adhesion performance. Particles with low mass and ductility have a high V_c to form coatings.

[0009] U.S. Pat. No. 6,759,085, Muehlberger, describes an improved cold spray process wherein the workpiece is placed in a low ambient pressure environment in which the pressure is substantially less than atmospheric pressure. The low pressure environment acts to substantially accelerate the sprayed powder particles, thereby forming an improved coating of the particles on the workpiece. An advantage is that the inert gas used in the process can be recycled easily. An inherent disadvantage is that a vacuum chamber is required.

[0010] In describing cold spray processing UK patent application GB 2,367,073 relates that experience indicates that the powder particles size should be in the range of about 10 to 50 microns to be suitable for cold spray deposition. This is because a high-pressure “bow” shock wave develops immediately adjacent to the substrate. This “bow shock” can begin to deflect and decelerate spray particles having a particle size below approximately 5 μm . UK patent application 2,394,479 also discusses the “bow shock” phenomena; indicating that below 5 μm in diameter, the particles of powder get swept away from the substrate due to a bow shock layer. There apparently is insufficient mass, and thus momentum, to propel the particle through the bow shock region. This lower limitation on particle size may be the reason that cold spray processing has not been demonstrated useful in preparing thin metal coatings, for instance, films less than about 8 microns. Alkhimov, in the “414 patent discloses an 8 μm coating formed at the lower deposition rate limit, below which no coating at all was deposited. In “Microstructural characteristics of cold-sprayed nanostructured WC—Co coatings” (Thin Solid Films 416, 2002, pp 129-135) Lima, et al, describe the formation of a 10 μm tungstencarbide-cobalt coating prepared from nanostructured materials using a cold spray process. The bow shock phenomenon was circumvented by agglomerating the nanoparticles into larger (about 10 to 43 μm) irregular shaped porous particles prior to the cold spray process. Cold spray processing with nitrogen gas gave a densely packed coating with some surface roughness.

[0011] Thin metal coatings are typically achieved with physical or chemical vapor deposition methods under vacuum and high temperature conditions, usually 250-1200° C. For repair of work pieces in the field, where a thin coating is required, vacuum or high temperature processing is not suitable. Other methods such as electroplating and brush-plating can be used to prepare thin coating, but they have toxicity and environmental issues associated with them. A cold spray process that allows the deposition of thin metal coatings in the range of 1 μm and higher would be useful in

repairing many functional coatings such as corrosion resistance coatings for aircraft, ships, boilers, bridges, and other steel structures. Disclosed herein are novel compositions and methods, using cold spray processing, for preparing thin metal coatings. The invention provides novel compositions comprising non-ductile hard spheres with fine metal powders adhered thereon, that can be used in a novel cold spray process to deposit fine metal powders onto a substrate.

SUMMARY OF INVENTION

[0012] One object of the invention is to adapt the cold spray process to provide a method of coating fine metal particles, of less than 5 μm average particle size, to a work piece. Another object of the invention is to provide a refurbishing method for applying thin metal coatings, of about 1 to about 10 μm in thickness, to a work piece. Another object of the invention is to provide metal coatings characterized by very small grain size, densely packed and work-hardened, to give wear resistant coatings.

[0013] In one embodiment, the invention is a metal agglomerated hard sphere composition capable of providing about a 1 μm or thicker coating of a metal on a work piece in a cold spray process comprising: a plurality of non-ductile hard spheres, said spheres comprised essentially of material characterized by an elongation at break of less than 7% at room temperature, and further characterized by an average sphere diameter of about 10 to 300 μm ; and about 0.1 to about 20 wt % metal powder comprising a plurality of metal particles characterized by an average particle size of about 10 nm to about 10 μm ; said plurality of metal particles being agglomerated onto said non-ductile hard spheres.

[0014] Another embodiment of the invention is method of coating metal particles, including metal particles having a particle size of about 0.01 to about 10 μm , onto a work piece surface with cold spray processing, comprising: mixing, into a gas stream characterized by a working pressure and working temperature, a metal agglomerated hard sphere composition to provide a particle-gas stream, wherein said metal agglomerated hard sphere composition comprises a plurality of non-ductile hard spheres, said spheres comprised essentially of material characterized by an elongation at break of less than 7% at room temperature, and further characterized by an average sphere diameter of about 10 to 300 μm ; and about 0.1 to about 20 wt % metal powder comprising a plurality of metal particles characterized by an average particle size of about 10 nm to about 10 μm , said plurality of metal particles being agglomerated onto said non-ductile hard spheres; accelerating said particle-gas stream into a supersonic jet; and directing said supersonic jet onto a work piece, wherein said metal agglomerated hard sphere composition impinges said work piece surface at sufficient velocity to deposit said metal particles from said non-ductile hard spheres onto said work piece surface, thereby coating said work piece surface with a desired thickness of metal particles to provide a metal coating.

BRIEF DESCRIPTION OF THE FIGURES

[0015] **FIG. 1** shows scanning electron microscope (SEM) photographs of coated particles. (a) 600 \times magnification; and (b) 2000 \times magnification showing a single coated hard sphere with the metal particles agglomerated on the surface.

[0016] **FIG. 2** illustrates schematically a cold spray apparatus useful in the invention.

[0017] **FIG. 3** is a cross section SEM photograph of an aluminum coating on 4130 steel substrate prepared using the process of the invention.

[0018] **FIG. 4** (a) and (b) are cross section SEM photographs of an aluminum coating with about 10 and 30 μm thickness prepared by cold spraying process of the invention.

DETAILED DESCRIPTION OF INVENTION

[0019] The metal agglomerated hard sphere composition of the invention, hereafter referred to as the agglomerate, except in the claims, is comprised of a plurality of non-ductile hard spheres. By spheres we mean that the particles are generally spherical in nature and have a ratio of shortest axis length to longest axis length in three dimensions that is approximately equal to 1, which is generally characteristic of a sphere. However, particles having some deviation from that relationship also may be useful. Preferably the spheres are solid particles. The spheres can be made of ceramic, metal or metal alloy having an average sphere diameter of about 10 to about 300 μm . Preferably the spheres have an average sphere diameter of about 50 to 100 μm and the spheres are comprised essentially of material characterized by an elongation at break of less than 7% at room temperature. Ceramic spheres preferably have a Mohs hardness of greater than 4.0 and preferably greater than 5.0. Metallic spheres preferably have a Rockwell hardness on the C scale of greater than 40.

[0020] Materials making up the non-ductile hard spheres include those selected from the group of: glass, including A-glass (soda-lime) and E-glass (borosilicate), titanium oxide, titanium nitride, aluminum nitride, aluminum oxide, zirconium oxide, magnesium oxide, scandium oxide, hafnium oxide, yttrium oxide, cerium oxide, garnet, steel and steel alloys. Most preferred materials for the spheres are glass, including A-glass (soda-lime) and E-glass (borosilicate), steel and steel alloys. Spherical materials that can function as non-ductile hard spheres are commercially available. For instance, PQ Corporation, Valley Forge, Pa. offers the brand name product SPHERIGLASS® solid glass spheres in the range of 7 to 200 μm ; Ceroglass Technologies offers soda lime glass beads in the 100 thru 400 mesh range with a Mohs hardness of 5.5-6.0, and a roundness of 65 to 95%. Stainless steel shot is available in 110 thru 330 mesh range with Rockwell hardness up to 52 from Ceroglass Technologies. A steel shot is available from International Surface Preparation with a 42-55 Rockwell hardness and a 200 to 300 μm diameter. Zirconium oxide-silicate ceramic (BSLZ series from Ceroglass Technologies) with a Mohs hardness ≥ 7.2 , 96% sphericity and a 70 to 300 μm particle size also is useful in the invention. Many other types and sources of hard spheres are known in the material arts and may be useful alternatives in practicing the invention.

[0021] The agglomerate is further comprised of metal powder that is agglomerated onto the surface of the non-ductile hard spheres. The metal powder is comprised of a plurality of metal particles characterized by an average particle size of about 10 nm to about 10 μm . Preferably the metal powder is characterized by average particle size of about 0.1 to about 5 μm and is comprised essentially of material characterized by an elongation at break greater than 10% at room temperature. The average particle size of the

metal powder is preferably about 10 to about 1000 times less than that of the non-ductile hard spheres. The metal powder preferably is selected from the group: aluminum, copper, nickel, zinc, cobalt, iron, titanium, silver, gold, chromium, tungsten, and alloys thereof; and the intermetallics titanium aluminide, iron aluminide and nickel aluminide. Most preferably the metal powder is selected from the group aluminum and copper.

[0022] Metal powders suitable for preparing agglomerates are commercially available. For instance, aluminum powder, 1 to 3 μm particle diameter, is available from Atlantic Equipment Engineers; copper powder, 1 to 2 μm particle size is available from Umicore Canada Inc.; cobalt powder with size ranging from 0.9 and 3.5 μm is available from Euro-tungstene Co.; copper-zinc alloy powder with size of 3-5 μm is available from Shieldinton Ind. PTE. LTD; tungstencarbide-cobalt alloy in nanometer scale (without agglomeration) is available from Sulzer-Metco, Westbury, N.Y.

[0023] The agglomerate can be formed by mixing a desired amount of metal powder with the hard spheres. The specific surface area (SSA) of the metal powder and hard spheres can be considered in formulating the agglomerate. However, typically it has been found more useful to empirically determine the most suitable ratio of hard sphere to metal powder. In general, too little metal powder results in a lost of production rate and too much powder causes flowability problems. Superfine powders and nano-powders often have flowability issues. They can be very difficult to convey through a hose at a uniform rate. A properly formulated agglomerate of the invention can circumvent this problem. A suitable ratio for a hard sphere-metal powder combination can be determined by running a trial coating of a selected ratio of hard sphere and metal powder and determining whether the composition gives a uniform coating. A non-uniform thickness of the metal coating, as measured with a coating thickness gauge is indicative of a flowability problem with the agglomerate. In this case, reducing the metal powder loading can often improve the uniformity of the coating. However, when too little metal powder is present in the agglomerate, the process suffers from reduced production rate. Preferably a metal agglomerated hard sphere composition comprises about 1 to about 10 wt % metal powder and more preferably about 4 to about 6 wt % metal powder. In the Example of aluminum powder and glass spheres, for instance, a 5 wt % of aluminum powder is about optimal for cold spray coating of aluminum films.

[0024] The agglomerate typically is formed by the physical adsorption or static charge attraction of metal particles to the non-ductile hard spheres. Other than thoroughly mixing the metal powder and hard spheres, no other processing is usually required. The mixing can be accomplished at room temperature, or preferably at elevated temperature. A rotary kiln is useful in preparing the agglomerate. Other mixing devices such as a V-Blender, manufactured by Patterson-Kelly, can be used for the purpose. The metal powder and hard spheres are mixed for a period of time sufficient to distribute the metal powder over the surface of the hard spheres. In general a period of 10 minutes to about 2 hours is sufficient time to establish a uniform distribution, although longer times periods may be used. The rotary kiln may be heated to a temperature in excess of ambient temperature during the agglomeration process. Usually a temperature of

about 50 to 200° C. is used, and preferably the kiln is heated to about 70 to about 150° C. The mixing process is usually accomplished under an inert atmosphere. Preferably a nitrogen or argon atmosphere is used to prevent oxidation of the reactive metal powders. **FIG. 1** is a scanning electron micrograph of a typical agglomerate of the invention showing glass spheres, **101**, with aluminum particles, **102**, adsorbed onto the surface.

[0025] Freshly prepared agglomerate can be sensitive to air and moisture that can lead to oxidation and/or poor flowability. For best results and performance the agglomerate should be protected from ambient atmosphere after preparation until it is sprayed.

[0026] Another embodiment of the invention is a method of coating about 10 nm to about 10 μm metal particles onto a work piece with cold spray processing. For the reasons described in the background of invention the particle size of metals useful in the cold spray coating of substrates is limited by the bow shock phenomenon. Small particles do not have the momentum necessary to impinge the substrate surface. The method of the invention uses non-ductile hard spheres as carriers of small metal particles that allow small particles to be deposited on the surface of the work piece. Thus, the method of the invention is suitable for preparing thin metal coatings, on the order of 1 μm and higher, onto work pieces. The coatings have high adhesion to substrates and have high density. Another advantage of the coatings is that they have a particularly small grain size due to the very small metal particles from which they are derived. Metal particles of nanometer scales, give coatings with grain size of similar scale because cold spray processing temperatures are much lower than the metal melting point, which does not give grain growth conditions.

[0027] Cold spray coating devices useful to practice the method of the invention are commercially available from Ktech Corporation, ASB Industries, Barberton Ohio, and the Obninsk Center for Powder Spraying in Russia. Alkhimov in the '414 patent, herein incorporated by reference, describes a useful apparatus for the invention.

[0028] **FIG. 2** shows a schematic of a cold spray apparatus useful for practicing the method of the invention. Compressed gas from a gas supply is supplied along a pneumatic line **201** in the direction **202** via shut-off and control valve **203**, gas distributor **204**, hose **205**, and valve **206**, pre-heated to a desired temperature with an in-line heater **207** and directed to a mixing chamber **210** via hose **208**. Agglomerate is added to one of multiple feed hoppers **220**, **221** and **222**, which are controlled by valves **217**, **218**, and **219**, respectively. The other two hoppers can hold steel balls and glass beads for cleaning and shot-peening processes, respectively. In normal operation only one hopper valve is open for a specific process. Usually the agglomerate is put into hopper **220** that is controlled by valve **217**. In the coating process, compressed gas enters the hopper **220** and carries the agglomerate, via valve **217**, to mixing chamber **210** through hose **223**. In the mixing chamber **210**, the agglomerate is mixed with the heated pressurized gas to provide a particle-gas stream. The particle-gas stream is accelerated into a supersonic jet by passing through a Laval nozzle, **211**. Thus, the particle-gas stream obtains sufficient velocity in the direction **212** for the agglomerate to deposit metal particles onto a work piece **214**, forming a coating **213**. The work

piece **214**, can be translated with an X-Y translation stage (not shown) that allows control of the area of the deposition. The non-ductile hard spheres that act as a carrier substantially bounce off the work piece and can be collected in the low pressure effluent from the process.

[0029] The pressurized gas accelerant is an important parameter in cold spray processing. Typically in cold spray processes, helium, or a mixture of helium and nitrogen, is used to accelerate particles with a size range of from 5 to about 50 μm . According to Alkhimov, helium is preferred because it has a very high sonic velocity, and larger particles can achieve V_c using it as an accelerant. Other gases including nitrogen, air, argon and the other noble gases, carbon dioxide and mixtures thereof can also be used effectively depending upon the ductility of the material, particle size and gas temperatures.

[0030] Particles larger than 50 micron typically can not achieve critical velocity required to bond to substrates, even in pure helium. However, U.S. Pat. No. 6,139,913, Van Steenkiste, et al., hereby incorporated by reference, describes a modified spray apparatus wherein particles greater than 50 μm can achieve the critical velocity (V_c) even in air, and are useful in forming a cohesive layer of particles. When the cross-sectional area ratio of the main heated air flow passage relative to the particle injection tube is at least 80:1, large particles can reach critical velocities. The apparatus described by Van Steenkiste in the '913 patent can be used for practicing the method of the invention.

[0031] The method of the invention can be accomplished using nitrogen, argon, or mixtures thereof, as the primary accelerating gas. Air can also be used in cases where non-reactive metals or metal alloys are to be coated. Preferred gases for the invention are argon, air, nitrogen and mixtures thereof. The compressed gas usually has a working pressure of about 70 to about 500 psi, depending upon the metal or alloy to be coated, nozzle type and the properties of the work piece. Preferably, the gas has a working pressure of about 90 to about 300 psi. The gas stream is heated, usually to a working temperature of about 30 to about 600° C., and preferably about 200 to 400° C., before it enters the mixing chamber, **210**. The heated gas allows for a higher velocity to be achieved in the supersonic jet and keeps the gas from rapidly cooling and freezing once it expands past the throat of the nozzle. U.S. Pat. No. 6,722,584, Kay, et al, hereby incorporated by reference, describes a convenient commercial source of a heating element, a Monel® 400 tube, wound in the form of a coil, and powered by a welding power supply. The same patent provides an improved design for a cold spray gun that can be used in the method of the invention.

[0032] The rate of addition of agglomerate to the mixing chamber is controlled by the hopper valve, **217**. The material hopper can be configured in several ways to deliver precise amounts of agglomerate to the mixing chamber. One configuration, described in the '414 patent, delivers precise amounts of powder that is picked up by a non-heated compressed gas stream and delivered to the mixing chamber. The rate of addition of agglomerate is a primary parameter used in controlling the rate of deposition of metal particles on the work piece. The optimal addition rate depends upon several parameters including the gas flow rate, the loading of metal powder, the type of material and thickness of the

coating desired. The optimal addition rate is determined empirically using several trials for each material. With a fixed work piece translation speed or jet translation speed, an optimal addition rate is that suitable for forming a uniform and desired thickness coating in one pass. The particle addition can be driven by a gas stream through a hose from powder hopper to the mixing chamber, while the addition rate is adjusted by a hopper valve **217**. Alternatively, several passes of the jet over a work piece can be made.

[0033] The particle-gas stream provided in the mixing chamber, **210**, accelerates by passing through a Laval nozzle, **211**, to form a supersonic jet that is directed at a work piece to be coated. The exit port of the nozzle is some working distance from the work piece, preferably 10 to about 30 mm and most preferably about 15 to 25 mm. An X-Y translation stage can move the work piece or, alternatively, the mixing chamber and Laval nozzle, to control the area of deposition, and the rate of movement controls the deposition per unit area. Repeated scanning of the work piece often can give more uniform coatings than a single pass. In field applications the mixing chamber and nozzle assembly can be a hand held, giving the operator the freedom to apply coating wherever desired.

[0034] The work piece can be selected from the group: metal, metal alloy, ceramic, organic polymer including dielectrics, concrete and wood.

[0035] The deposition efficiency of the process depends on the type of the metal particles and hard spheres, nozzle type, substrate material, and gas temperature and gas pressure that are related to particle velocity. Compared to the conventional cold spray method, there are two velocities of issue in this process. Usually if the particle velocity is too low, the hard spheres do not have sufficient energy to cause the metal particles to deform plastically, resulting in poor deposition efficiency. If the particle velocity is too high, the hard spheres tend to abrade the surface, removing coating rather than depositing it. Thus, for the process of the invention, there is a minimum critical velocity (V_c) and a maximum velocity (V_m) between which is an optimum velocity (V_o) that, at a specific temperature, gives an optimum deposition efficiency. In practical situations, monitoring gas pressure is much easier than monitoring gas-particle stream velocity. Thus, gas pressure and temperature are the parameters most often used to control particle velocity; and too low or too high particle velocity can result in low deposition efficiency.

[0036] The process of the invention has several advantages. (1) helium is not required to attain critical velocity for coating. Often compressed air is preferred if the coating particle does not react with air. (2) Fine particle size metal powders may be used—even nano-sized particles. The hard spheres carry the powder to the substrate surface, thus overcoming the bow-shock effect. The process allows cold spraying of nano-particles to form dense nano-structured coatings. (3) High pressure for superfine particle deposition is not necessary. The energy required for plastic deformation of the metal particles is derived from the kinetic energy of the total agglomerate. (4) Coatings derive from the process have higher wear resistance. The hardness of the coating is greater than its counterpart bulk material and greater than the same coating prepared by conventional cold spray.

[0037] The method of the invention can be used in combination with pre-cleaning processes. For instance, the work

piece can be treated with a gas stream with entrained abrasive agent prior to the coating process to remove contaminants and provide a fresh surface for bonding. For the cleaning process, a second material hopper, **221**, communicating with the mixing chamber, **210**, may contain the abrasive agent including those selected from the group: glass spheres, sand, alumina, silicon carbide, and steel spheres.

[0038] The method of the invention can further be combined with a shot-peening process to further densify the metal coating. A third material hopper, **222**, communicating with the mixing chamber, **210**, can contain the shot-peening agent including those selected from the group: steel shot, glass beads and other non-ductile spheres with a particle diameter of about 10 to about 100 μm . The gas pressure can be adjusted to accommodate, pre-cleaning, coating, and shot-peening.

[0039] Although the invention is not meant to be limited by any mechanism or mode of action, the following explanation may convey some understanding of the process. When the agglomerate impinges the work piece surface at a sufficient velocity, metal particles transfer from the non-ductile hard spheres to the work piece surface, the non-ductile spheres acting as a hammer, applying significant kinetic energy to the ductile metal particle. The non-ductile hard spheres substantially bounce off the work piece and are swept away in the effluent gas stream. Coating cross-sections characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) typically show very little hard sphere residue. For instance, **FIG. 3** shows a cross-section of a sample in which an aluminum coating **301** is on the surface of a 4130 steel substrate **302**. Material **303** is the mounting polymer for SEM sample preparation. The aluminum coating is about 5 μm thick and of substantially uniform thickness. The substrate interface and the coating surface are irregular that is probably an inherent trait of the pre-cleaning and the coating process.

[0040] The method of the invention can provide uniform coatings with a thickness of about 1 μm up to 40 μm or more. Thin metal coatings usually are provided by vapor/ion deposition or electroplating/brush-plating methods. The opportunity to use cold spray processes to provide thin coatings is a significant advantage in refurbishing corrosion resistant coatings. Another advantage of the method of the invention is that the coatings are made by compacting very small metal particles, on the order of 10 nm to 10 μm . Thus, the grain size of the coatings can be very small. Properties such as hardness, wear resistance and strength are influenced by grain size, grain structure and the metal or metal alloy types.

[0041] The following examples are meant to give guidance on specific parameters that can be used to practice the invention and are not meant to define or limit the invention.

EXAMPLE 1

[0042] This example illustrates the formation of an agglomerate of the invention using aluminum as the metal powder.

[0043] A mixture of glass spheres (142.5 g, 170-400 mesh soda lime glass, Ceroglass Technologies Inc., Columbus Tenn.) and aluminum powder (7.5 g, 1-3 μm , Atlantic Equipment Engineers, Bergenfield, N.J.) was mixed (25

rpm) in a Reetz rotary furnace (HTM Reetz GmbH, Germany) for 0.5 h at 80° C. under an argon flow (0.5 L/min). The agglomerate was used directly in the cold spray process.

EXAMPLE 2

[0044] This example illustrates the formation of an agglomerate of the invention using copper as the metal powder.

[0045] A mixture of glass spheres (138.5 g, 170-400 mesh soda lime glass) and copper powder (12.5 g, 1.5-3 μm , Umicore Canada, Inc., Canada) is mixed (25 rpm) in a Reetz rotary furnace for 0.5 h at 70° C. under an argon flow (0.5 L/min).

EXAMPLE 3

[0046] In a similar manner to Example 1, nickel powder (7.5 g, 50-100 nm, Tekna RF Plasma Equipment, Canada) is treated with glass spheres (142.5 g) at room temperature.

EXAMPLE 4

[0047] In a similar manner to Example 1, cobalt powder (7.5 g, average particle size 1.25 μm , Eurotungstene Co., Grenoble, France) is treated with glass spheres (142.5 g) at 70° C.

EXAMPLE 5

[0048] This example illustrates the formation of a thin aluminum coating on a steel substrate using the process of the invention.

[0049] A 4130 steel coupon (1×4 in) was mounted on a X-Y table of the 3-D motion stage (Mill **2000**, Flashcut CNC Inc., Deerfield, Ill.) controlled by a computer. The agglomerate, from Example 1, was loaded into a material hopper of a DIMET 402 cold spray apparatus. The standard nozzle was installed on the Z-axis of the 3-D stage about 15 mm working distance from the steel coupon and at an incident angle of 90 degrees. Argon gas (105 psi) was preheated to about 400° C. and directed to the mixing chamber. The agglomerate was fed to the mixing chamber at about 10 g/min. The coupon was translated at about 20 in/min in one pass under the nozzle to give about a 5 μm aluminum coating.

[0050] SEM (model JEM-840A, JEOL, Japan) and EDS (Model: Inca Energy, Oxford Instruments, UK) analysis of the aluminum coating were performed. The SEM of the coating is shown in **FIG. 3**. EDS analysis of the aluminum coating shows about 99% elemental aluminum in the composition spectrum.

EXAMPLE 6

[0051] The following example illustrates the process of the invention combined with a preliminary cleaning process and a shot-peening process after the coating process of the invention.

[0052] A 4130 steel coupon (1×4 in) with an organic polymer coating (about 500 μm) was mounted on the X-Y table of the 3-D motion stage controlled by a computer. A glass bead composition (soda lime, 170-400 mesh, Mohs 5.5-5.6) was loaded into a material hopper of the cold spray apparatus. The spray nozzle was installed on the Z-axis of

the 3-D stage about 25 mm working distance from the steel coupon and at an incident angle of 80 degrees. Air (75 psi), at room temperature, was directed to the mixing chamber. The glass bead composition was fed to the mixing chamber at about 10 g/min. The coupon was translated at about 20 in/min in two passes under the nozzle to give a substrate free of any organic coating. Using steel shot (100-300 μm , International Surface Preparation, Houston, Tex.), one pass was necessary to give a substrate free of any organic coating.

[0053] The coupon was coated with aluminum using parameters outlined in Example 5, with the exception that the agglomerate feed rate was 18 g/min, to give a 10 μm coating. A second coupon, using an agglomerate feed rate of 30 g/min, was coated to provide a 30 μm coating.

[0054] The two coated coupons were shot-peened. The same glass bead composition as described above was sprayed (10 g/min) with air (40-45 psi) at room temperature with a 25 mm nozzle working distance at an incident angle of 80 degrees. The coupons were translated at about 20 in/min in one pass.

[0055] After shot-peening the coated coupons were cut for SEM samples. **FIG. 4 (a)** is an SEM of the coupon showing a 10 μm aluminum coating, **401**, on a steel substrate, **402**. **FIG. 4 (b)** is an SEM of the coupon showing a 30 μm aluminum coating **403**, on a steel substrate, **404**.

[0056] Coating adhesion tests were made following the instructions in standard MIL-DTL-83488D, using the Scrape and Bending methods. In the scrape test, the surfaces of several aluminum coatings of different thickness were scraped with a diamond needle to expose the base metal. Samples were prepared for SEM and EDS analysis. EDS analysis confirmed that the bottom of the scraping line was the substrate metal. SEM photographs showed no evidence of non-adhesion in all samples. In the bending test, coated coupons, with dimensions of 1 \times 4 in, were clamped in a vise and bent back and forth until strip rupture occurred. The coupons were tested with different coating thickness in the range of 6-30 μm . The rupture area was cut down from the coupons as SEM samples. SEM observation showed no evidence of delamination in the ruptured area, and the separation between the coating and the base metal occurred at the point of rupture.

EXAMPLE 7

[0057] A commercial ceramic tile (2 \times 2 in) is coated with copper using the agglomerate prepared in Example 2 and the method outlined in Example 5, with the exception that the agglomerate feed rate is about 20 g/min, to give about a 10-20 μm copper coating.

EXAMPLE 8

[0058] A steel coupon (1 \times 4 in) is coated with nickel using the agglomerate prepared in Example 3 and the method outlined in Example 5, with the exception that the agglomerate feed rate is about 20 g/min, to give about a 10-20 μm nickel coating.

EXAMPLE 9

[0059] A steel coupon (1 \times 4 in) is coated with cobalt using the agglomerate prepared in Example 4 and the method

outlined in Example 5, with the exception that the agglomerate feed rate is about 20 g/min, to give about a 10-20 μm cobalt coating.

[0060] It is understood that the above-described embodiments of the invention are illustrative only and modification thereof may occur to those skilled in the art. Accordingly, it is desired that this invention is not to be limited to the embodiments disclosed herein but is to be limited only as defined by the appended claims and their legal equivalents.

I claim:

1. A metal agglomerated hard sphere composition capable of providing about a 1 μm or thicker coating of a metal on a work piece in a cold spray process comprising: a plurality of non-ductile hard spheres, said spheres comprised essentially of material characterized by an elongation at break of less than 7% at room temperature, and further characterized by an average sphere diameter of about 10 to 300 μm ; and about 0.1 to about 20 wt % metal powder comprising a plurality of metal particles characterized by an average particle size of about 10 nm to about 10 μm , said plurality of metal particles being agglomerated onto said hard spheres.

2. A metal agglomerated hard sphere composition of claim 1, wherein said non-ductile hard spheres have an average sphere diameter of about 50 to about 100 μm .

3. A metal agglomerated hard sphere composition of claim 1 wherein the non-ductile hard spheres are comprised essentially of material selected from the group: glass, including A-glass (soda-lime) and E-glass (borosilicate), titanium oxide, zirconium oxide, magnesium oxide, scandium oxide, hafnium oxide, yttrium oxide, cerium oxide, garnet, steel and steel alloys.

4. A metal agglomerated hard sphere composition of claim 2, wherein the non-ductile hard spheres are comprised essentially of material selected from the group: A-glass (soda-lime), E-glass (borosilicate), steel and steel alloys.

5. A metal agglomerated hard sphere composition of claim 1, wherein said composition comprises about 1 to about 10 wt % metal powder.

6. A metal agglomerated hard sphere composition of claim 4, wherein said composition comprises about 4 to about 6 wt % metal powder.

7. A metal agglomerated composition of claim 1, wherein the metal powder is selected from the group of aluminum, copper, nickel, zinc, cobalt, iron, titanium, silver, gold, chromium, tungsten, and alloys thereof, and the intermetallics titanium aluminide, iron aluminide and nickel aluminide.

8. A metal agglomerated composition of claim 1, wherein the metal powder is selected from the group of aluminum and copper.

9. A metal agglomerated composition of claim 6, wherein the metal powder is selected from the group of aluminum and copper.

10. A metal agglomerated composition of claim 1, wherein said metal powder is characterized by an average particle size of about 0.1 to about 5 μm and is comprised essentially of material characterized by an elongation at break greater than 10% at room temperature.

11. A metal agglomerated hard sphere composition of claim 2 wherein the non-ductile hard spheres are comprised essentially of A glass (soda-lime), and said composition comprises 4 to about 6 wt % aluminum powder character-

ized by a purity of greater than 99.0% and an average particle size of about 0.1 to about 5 μm .

12. A method of coating metal particles, including metal particles having a particle size of about 0.01 to about 10 μm , onto a work piece surface with cold spray processing, comprising:

mixing, into a gas stream characterized by a working pressure and working temperature, a metal agglomerated hard sphere composition to provide a particle-gas stream, wherein said metal agglomerated hard sphere composition comprises a plurality of non-ductile hard spheres, said spheres comprised essentially of material characterized by an elongation at break of less than 7% at room temperature, and further characterized by an average sphere diameter of about 10 to 300 μm ; and about 0.1 to about 20 wt % metal powder comprising a plurality of metal particles characterized by an average particle size of about 10 nm to about 10 μm , said plurality of metal particles being agglomerated onto said hard spheres;

accelerating said particle-gas stream into a supersonic jet; and

directing said supersonic jet onto a work piece, wherein said metal agglomerated hard sphere composition impinges said work piece surface at sufficient velocity to deposit said metal particles from said non-ductile hard spheres onto said work piece surface, thereby coating said work piece surface with a desired thickness of metal particles to provide a metal coating.

13. A method of claim 12 wherein said pressurized gas is selected from the group: nitrogen, air, helium, argon, other noble gases, carbon dioxide, and mixtures thereof.

14. A method of claim 13 wherein said pressurized gas is selected from the group: nitrogen, air, argon, and mixtures thereof.

15. A method of claim 12 wherein accelerating said particle-gas stream into a supersonic jet, is provided for by passing said particle-gas stream through a Laval nozzle.

16. A method of claim 14 wherein accelerating said particle-gas stream into a supersonic jet, is provided for by passing said particle-gas stream through a Laval nozzle.

17. A method of claim 12 wherein said working pressure is about 70 to about 500 psi and said working temperature is about 30 to about 600° C.

18. A method of claim 16 wherein said working pressure is about 90 to about 300 psi and said working temperature is about 200 to 400° C.

19. A method of claim 12 wherein said non-ductile hard spheres have an average sphere diameter of about 50 to about 100 μm and are comprised essentially of material selected from the group: A-glass (soda-lime), E-glass (borosilicate), steel and steel alloys.

20. A method of claim 18 wherein said non-ductile hard spheres have an average sphere diameter of about 50 to about 100 μm and are comprised essentially of material selected from the group: A-glass (soda-lime), E-glass (borosilicate), steel and steel alloys.

21. A method of claim 12, wherein said non-ductile hard spheres are comprised essentially of A-glass (soda-lime).

22. A method of claim 20, wherein said non-ductile hard spheres are comprised essentially of A-glass (soda-lime).

23. A method of claim 12 wherein said wherein said metal agglomerated hard sphere composition comprises about 1 to about 10 wt % metal powder.

24. A method of claim 12 wherein said wherein said metal agglomerated hard sphere composition comprises about 4 to about 6 wt % metal powder.

25. A method of claim 22 wherein said metal agglomerated hard sphere composition comprises about 4 to about 6 wt % metal powder.

26. A method of claim 12, wherein said metal powder is selected from the group of aluminum, copper, nickel, zinc, cobalt, iron, titanium, silver, gold, chromium, tungsten, and alloys thereof; and the intermetallics titanium aluminide, iron aluminide and nickel aluminide.

27. A method of claim 12, wherein said metal powder is selected from the group of aluminum and copper.

28. A method of claim 25, wherein said metal powder is selected from the group of aluminum and copper.

29. A method of claim 12, wherein said metal powder is characterized by an average particle size of about 0.1 to about 5 μm and is comprised essentially of material characterized by an elongation at break greater than 10% at room temperature.

30. A method of claim 28, wherein said metal powder is characterized by an average particle size of about 0.1 to about 5 μm .

31. A method of claim 12 wherein said work piece comprises material selected from the group: metal, metal alloy, ceramic, organic polymer including dielectrics, concrete and wood.

32. A method of claim 31 wherein said work piece comprises aluminum coated steel.

33. A method of claim 28 wherein said work piece comprises aluminum coated steel.

34. A method of claim 12 comprising the additional and preliminary step of cleaning said work piece surface by providing a stream of non-ductile hard particles in a carrier gas, said particles characterized by an average particle diameter of about 10 to about 300 μm and selected from the group of: ceramic material having a Mohs hardness greater than 4.0 and metallic material having a Rockwell hardness on the C scale greater than 40; said stream being directed onto said work piece surface at a velocity sufficient to abrade said work piece surface to provide a clean work piece surface.

35. A method of claim 33 comprising the additional and preliminary step of cleaning said work piece surface by providing a stream of non-ductile hard particles in a carrier gas, said particles characterized by an average particle diameter of about 10 to about 300 μm and selected from the group of: ceramic material having a Mohs hardness greater than 4.0 and metallic material having a Rockwell hardness on the C scale greater than 40; said stream being directed onto said work piece surface at a velocity sufficient to abrade said work piece surface to provide a clean work piece surface.

36. A method of claim 12 comprising the additional step of shot-peening said metal coating by providing a stream of non-ductile hard particles in a carrier gas, said particles characterized by an average particle diameter of about 10 to about 300 μm and selected from the group of: ceramic material having a Mohs hardness greater than 4.0 and metallic material having a Rockwell hardness on the C scale greater than 40; said stream being directed onto said work

piece surface at a velocity sufficient to densify said metal coating and/or act to modify said coating thickness.

37. A method of claim 35 comprising the additional step of shot-peening said metal coating by providing a stream of non-ductile hard particles in a carrier gas, said particles characterized by an average particle diameter of about 10 to about 300 μm and selected from the group of: ceramic material having a Mohs hardness greater than 4.0 and metallic material having a Rockwell hardness on the C scale greater than 40; said stream being directed onto said work

piece surface at a velocity sufficient to densify said metal coating and/or act to modify said coating thickness.

38. A metal coating derived from the method of claim 12.

39. A metal coating of claim 38 wherein said metal powder is selected from the group of aluminum and copper.

40. A metal coating of claim 39 wherein said work piece comprises material selected from the group: metal, metal alloy, ceramic, organic polymer including dielectrics, concrete and wood.

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