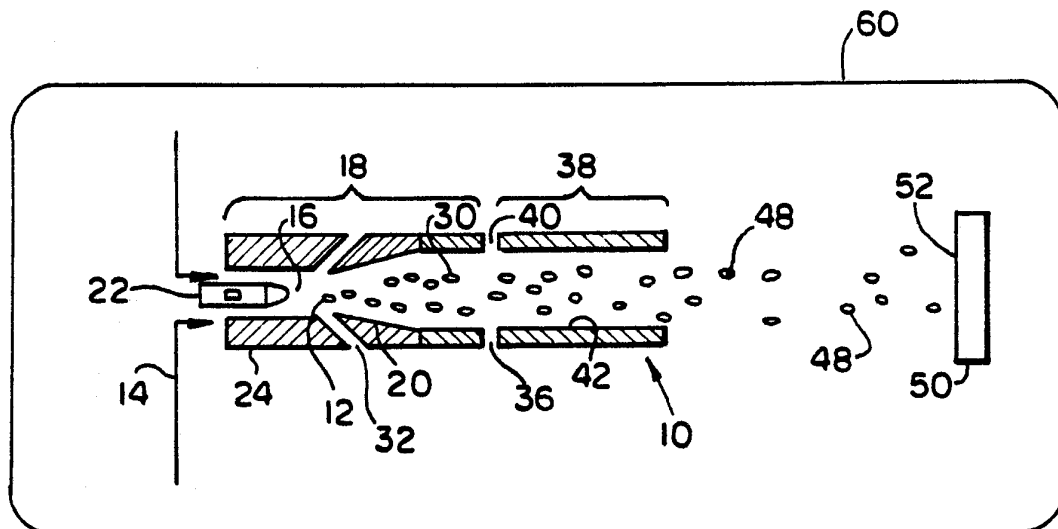




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<p>(21) International Application Number: PCT/US92/01132 (22) International Filing Date: 12 February 1992 (12.02.92) (30) Priority data: 656,886 15 February 1991 (15.02.91) US (71) Applicant: DREXEL UNIVERSITY [US/US]; 32nd & Chestnut Street, Philadelphia, PA 19104 (US). (72) Inventors: SMITH, Ronald, W. ; 1162 Horseshoe Drive, Blue Bell, PA 19422 (US). MATASIM, Zaher, Z. ; 513 Windsor Court, Apt. A-1, Andalusia, PA 19020 (US). (74) Agents: SCHWARZE, William, W. et al.; Panitch Schwarze Jacobs & Nadel, 1601 Market Street, 36th Floor, Philadelphia, PA 19103 (US).</p>		<p>(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report.</i></p>

(54) Title: METHOD AND APPARATUS FOR GAS PHASE DIFFUSION ALLOYING



(57) Abstract

A method and apparatus are provided for gas phase alloying of a molten metal or molten ceramic with an element (44) dissociated from a reactive gas (36). A plasma gun (18) is used to create a high temperature stream of inert which substantially liquefies metal or ceramic particles (30) injected into the stream. The plasma gun (18) is equipped with a reactor (38) wherein a reactive gas (36) is injected into the stream containing the metal or ceramic particles (30). At least one element dissociated from the reactive gas (36) reacts with the liquid metal or ceramic particles (30) suspended in the stream by diffusing into the liquid particles (30) to form a compound of the metal or ceramic and the element in at least a portion of the particles. The thus alloyed particles may be frozen and collected as particles or dispersed onto a substrate (50) and cooled to form a coating.

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5 **METHOD AND APPARATUS FOR**
 GAS PHASE DIFFUSION ALLOYING

Field of the Invention

 The invention relates to a method and
 apparatus for gas phase diffusion alloying of a
 material and, more particularly, for plasma spray-
10 forming and synthesizing coatings and near net-
 shape, substantially homogeneous, dense alloys
 having improved mechanical properties and wear
 resistance.

Background of the Invention

15 Continuing advances in the aerospace and
 power generation industries, to name a few, require
 the development of materials having increased
 temperature capabilities, wear resistance, and high
 strength-to-weight ratios. The formation of such
20 high performance materials may be prohibitively
 expensive. Further, the post-processing machining
 of such alloys is often difficult.

 Attempts have been made to enhance the
 properties of materials by particulate processing
25 (P/M), in which a material is mechanically mixed
 with a reactive material such as carbon or carbides
 prior to sintering of the mixture. The resulting
 materials were unsatisfactory because of non-
 uniform distribution of the resulting reacted
30 products in the material matrix.

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In a conventional spray-forming process, a two-fluid atomizer is used to atomize a molten metal alloy with an inert gas. Droplets of molten alloy cool and partially solidify during spraying, and splatter when projected onto a substrate. The accumulating droplets form a solid layer having a fine grain size and relatively low porosity. However, in this process, the molten metal alloy to be sprayed must have the same composition as the final product. Conventional spray-forming does not allow for synthesis of materials. This spray-forming process is not suitable for use with reactive metals because of difficulties in forming a reactive metal spray.

A refinement on the spray-forming process is spray casting, or the OspreyTM process. In the spray-casting process, a stream of molten metal is atomized with an atomizing gas to produce a spray of liquid droplets. The atomizing gas comprises an inert gas and may further include a reactive component such as oxygen or methane for reaction with the molten metal. For example, this method has been used to produce dispersions of aluminum oxide and titanium carbide in ferrous matrices. Alternatively, particles containing reactive elements such as carbon or boron, in solution, may be injected into the spray.

The temperature at which the OspreyTM process is carried out is not sufficient to dissociate a reactive gas into ions. This process is not suitable for use with refractory metals or ceramics. The droplets formed in the OspreyTM process are larger than the particles formed in the present method and reacted material is not as

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finely dispersed in the matrix. The OspreyTM process is carried out in bulk and is not suitable for coating particles and producing powders and films.

5 Reinforced alloys having high strength and modulus and good elevated temperature stability may be formed by an in-situ vapor-liquid-solid (VLS) process, as discussed in U.S. Patent No. 4,808,372 of M. Koczak et al. Gas is introduced
10 into a molten composition comprising a matrix liquid and at least one refractory carbide-forming component. A reactive component is also provided which reacts with the refractory component to form a refractory material dispersed in the matrix
15 liquid. The liquid is cooled to form a solid composite material.

The VLS process is not well-suited for ionizing a reactive gas nor for use with reactive metals. The present method provides a much greater
20 particle surface area and enhanced mixing to produce a more homogeneous and finely distributed product at a faster rate.

Another spray-forming process is plasma spraying. Plasma spraying involves introducing a
25 powdered material such as a metal into high temperature inert plasma, such as the plasma generated by a plasma gun. The powder rapidly melts and is projected onto a cool substrate. This process has a number of drawbacks. First, the
30 powder must be of the same composition as the desired product, thereby eliminating the possibility of synthesizing materials. Plasma-spray forming is carried out at rates substantially less than those of conventional spray-forming

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processes and is therefore less efficient. Plasma spraying is most often employed for application of coatings or formation of small near net-shape products.

5

Summary of the Invention

One aspect of the present invention comprises a method for gas phase diffusion alloying of a material. The material may be selected from the group consisting of metals and ceramics. Solid particles of the material are injected into a high temperature inert gas stream, or plasma jet. The temperature of the jet is sufficient to substantially liquefy the particles. A reactive gas is injected into the high temperature stream for dissociation and reaction with the particles while the particles are suspended in the stream and are at least partially in a liquid state. Preferably, the reactive gas is injected into the stream after the stream has been heated to the high temperature. At least one element of the reactive gas diffuses into the liquid particle to form a compound of the material and the element in at least a portion of the particle. Finally, the alloyed material is cooled. The plasma jet may propel the alloyed material against a substrate while the material is still partially liquid and thereby disperse the compound and material as a coating on the substrate. Alternatively, the alloyed material may be collected as a coated particle.

Another aspect of the invention relates to an apparatus for high temperature gas phase diffusion alloying of an element with a material

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selected from the group consisting of metals and ceramics. The apparatus includes a means for supplying a stream of inert gas and a means for heating the gas to a temperature sufficient to
5 liquefy particles of the material. Preferably the supply and heating means comprise a plasma gun. The apparatus further includes means for injecting solid particles of the material into the heated stream. Means for injecting a reactive gas
10 containing the element into the heated stream are also provided, the heated stream having a temperature sufficient to dissociate the reactive gas. The particle-injecting means and the reactive gas-injecting means are positioned relative to the
15 heated stream so that the reactive gas will not react with the heating means but will dissociate the reactive gas for diffusion of the element into the particles while the particles are at least partially in a liquid state. Finally, the
20 apparatus includes means for cooling the alloyed material, preferably by directing the stream into an environmentally controlled area and collecting the particles in a collection system or depositing the particles on a substrate.

25 Brief Description of the Drawings

The foregoing summary, as well as the following detailed description of the preferred embodiment, will be better understood when read in conjunction with the appended drawings. For the
30 purpose of illustrating the invention, there are shown in the drawings embodiments which are presently preferred, it being understood, however, that the invention is not limited to the specific

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arrangements and instrumentalities disclosed. In the drawings:

Fig. 1 is a schematic diagram of a portion of the gas phase diffusion alloying process in accordance with the present invention;

Fig. 2 is a simplified representation of the particulate/reactive gas phase reaction and consolidation in accordance with the present invention.

Fig. 3 is a schematic diagram of a process chamber and plasma gun for high temperature gas phase diffusion alloying in accordance with the present invention; and

Fig. 4 is a cross-sectional side view of a suitable plasma gun and plasma reactor for gas phase diffusion alloying in accordance with the present invention.

Detailed Description of the Preferred Embodiment

Referring to the drawings, wherein like numerals indicate like elements throughout, there is shown in Fig. 1 a diagram of the preferred method for gas phase diffusion alloying. This method will be discussed with reference to a schematic apparatus 10, it being understood, however, that the method may be carried out with apparatuses having various configurations in keeping with the spirit and scope of the present invention.

The material 12 to be alloyed is provided in the form of particles of materials selected from the group consisting of metals and ceramics. The material 12 must possess a melting point and must not decompose at reaction temperatures on the order

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of 5000°K to 10,000°K. Preferably, the material 12 is selected from the group consisting of transition metals, aluminum, silicon, and combinations and oxides thereof. Examples of transition metals
5 which may be used in accordance with the present method are tungsten, titanium, molybdenum, aluminum, niobium, nickel, chromium, cobalt, iron, hafnium, and yttrium. Ceramics for use in the present method include alumina, titania, yttria,
10 and zirconia, it being understood, however, that the present method is not limited to use with only the examples set forth above.

Referring now to Fig. 1, the method comprises providing a high temperature stream 14 of
15 inert gas, preferably a plasma jet 16. It is preferred that the jet be provided by a direct current (d.c.) plasma gun 18 (best shown in Fig. 4), although the jet may be provided by a radio frequency induction coupled discharge or other
20 suitable means. In the plasma gun 18, the stream 14 is heated and expanded through a nozzle 20 (see Fig. 4) to form an intense plasma jet 16 having core temperatures which may reach up to 20,000°K. Preferably, the plasma gun 18 heats
25 the plasma jet 16 to temperatures ranging from 5,000°K to 20,000°K.

A suitable plasma gun 18 is a 120 kW plasma spray system commercially available from Electro-Plasma as Model No. 03CA. The gun 18 is
30 equipped with gas spray nozzle 20 (Electro-Plasma Model No. 93). The gun 18 includes a cathode 22 and an anode 24 for forming a direct current arc (not shown). The cathode 22 may be formed from thiorated tungsten and the anode 24 from copper,

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although one skilled in the art would understand that the cathode 22 and anode 24 may be formed from other highly conductive materials. The gun 18 may be actuated by a torch manipulator 26 (see Fig. 3) to facilitate deposit of the alloyed material onto a substrate 50, if desired. The torch manipulator 26 may be controlled by a conventional controller (not shown) and may be powered by conventional means well within the knowledge of those skilled in the art. The plasma jet 16 is electrically neutral but contains many thermally excited atomic states of the typically inert gas.

The inert gas provides a medium for carrying out the reaction and for transferring energy to heat the reactants and propagate the reaction. For example, the inert gas may be selected from the group consisting of argon, helium, hydrogen, nitrogen and combinations thereof. Helium and hydrogen gases may be included in the inert gas to increase the enthalpy and heat transfer in the stream 14. The selection of an inert gas may be influenced by the melting point of the material. For example, a mixture of argon and hydrogen may be used with a material having a high melting point such as C103, a niobium alloy ($\text{Nb}_{10}\text{HfTi}$) which has a melting point of 2400°C. For a material having a lower melting point, such as titanium which has a melting point of 1670°C, the mixture of inert gases may be argon and helium. One skilled in the art would understand that other inert gases or even air may be used so long as undesired side reactions are minimized in keeping with the spirit and scope of the present invention.

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Preferably the flow rate of the inert gas stream 14 ranges from 140 scfh to 400 scfh, although one skilled in the art would understand that the flow rate may vary based upon a number of factors, such as the flow rates of the reactant streams, spray distance, material particle size and melting point, input temperatures of the reactants, etc.

The method further comprises means for injecting solid particles 30 of the material 12 into the plasma jet 16. The particles are injected through inlet ports 32 in the plasma gun 18, as shown in Figs. 1 and 4. The inlet ports 32 are preferably located proximate the upstream end of the nozzle 20.

As best shown in Fig. 3, the particles 30 are preferably fed through a powder feeder 34 which is controlled by a controller (not shown). The preferred powder feeder 34 is an EPI volumetric feeder, however one skilled in the art would understand that one of many different types of feeders, too numerous to mention, could be employed.

The particles 30 are preferably injected with a carrier gas 28 (see Fig. 3) to facilitate injection. The carrier gas 28 is preferably an inert gas, such as argon. Typically the particles 30 and carrier gas 28 are not preheated prior to injection, although they may be. The particles 30 are injected with the carrier gas 28 into the hot plasma jet 16 where the particles 30 melt. The flow rates of particles and carrier gas are not particularly critical to the present invention and will depend upon such factors as the

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particular apparatus employed, the plasma gas flow rate and the particular reaction and application being performed.

The diameter of the material particles 30 typically ranges from 5 to 45 microns, although greater conversion may be obtained using particles less than 5 microns. Smaller particles possess a higher surface-to-volume ratio, which enhances the reaction, and may be used where more complete alloying (as contrasted with coating) is desired.

The stream of inert gas must be heated to a temperature sufficient to substantially liquefy or melt the particles of material.

Referring now to Fig. 1, the method further comprises injecting a reactive gas 36 into the plasma jet 16. Preferably, the plasma gun 18 is equipped with a reactor 38 (see also Fig. 4). The reactor 38 has inlet ports 40 in its walls 42, through which the reactive gas 36 is injected into the plasma jet 16. The reactive gas may be injected countercurrent to the flow of the plasma jet 16 to enhance mixing and reaction. It is preferred that the reactive gas be injected radially with a tangential swirl component. Preferably, the reactor 38 is shaped in the form of a cylindrical tube.

The reactive gas 36 is comprised of at least one element 44 which dissociates or ionizes in the high temperature plasma jet 16. Examples of element 44 include silicon, nitrogen, carbon, oxygen, boron, fluorine, or sulfur, to name a few, which are reacted with particles of the material to form a coating or film of carbides, carbo-nitrides, silicon carbide, oxides, or fluorides on the

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particles. The uniformity of the surface coating depends on the size of the molten particles 30, the particle surface temperature, and the diffusion of reactive gas element(s) 44 into the particle.

5 Suitable reactive gases 36 include, for example, methane, propylene, fluorine, nitrogen, acetylene, disilane, boron trifluoride, oxygen, and combinations thereof. One skilled in the art would understand that other reactive gases comprising
10 various other reactive elements may be used in the keeping with the spirit and scope of the present invention.

As best shown in Fig. 2, at least one element 44 of the reactive gas 36 diffuses into the
15 liquid particle 30 to form a compound of the material and the element in at least a portion of the particle 30, thereby forming a film on the particle 30. The thickness of the film is generally greater than 0.005 microns. The center
20 of the particle remains molten and the film takes the form of a hardened shell. It will be understood that Fig. 2 is a highly simplified representation and that elements 44 form a diffusion coating on the particles, and actually
25 penetrate the particles 30 to react with the material and form compounds between the elements 44 and the materials 12. Atoms of the elements migrate toward the center of the particles 30 to form alloys in the material matrix with a
30 decreasing concentration gradient from the surface toward the center.

As used herein, the term "alloyed" in reference to the material, after reaction of the element with the material particle and diffusion of

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the element into the particle, is intended to include both reacted states (i.e., where a compound of the element and material are formed) and alloyed states (i.e., where the element is present in the material matrix but does not actually form a compound). It will be understood by those skilled in the art of diffusion coatings that a gradient of these "alloyed" states will exist in the particle from surface to center.

10 In one embodiment (shown in the figures 1 and 2) the plasma jet 16 propels the particles 48 of alloyed material against a substrate 50, causing the particles 48 to flatten and adhere to the substrate 50 or onto prior deposited particles 48.

15 The velocity of the particles 48 at impact may typically be in the range of several hundred m/s. The film covering the particle of reacted material ruptures and produces on the substrate surface 52 a deposit of dispersoids 54 of the compounds

20 comprised of reacted elements and the material 12, unreacted elements, if any, and unreacted material. The density and microstructure of the dispersion are influenced by the temperature profiles of the plasma jet and the particle trajectories within the plasma jet and the reactor which determine each

25 particle's degree of melting. The degree of conversion of the surface of each particle also depends on the concentration of reactive gas as well as the residence time during which the

30 particles and the elements are in contact.

The dispersoids reinforce the material matrix to increase the capability of the material to withstand elevated temperatures, wear, high stress, or combinations thereof while increasing

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the strength-to-weight ratio. This method allows the formation of near net-shape spray-formed structures eliminating costly and difficult machining of the alloyed material.

5 Alternatively, a free-fall cooling zone may be provided with a powder collection system 64 as in Figure 3 to respectively freeze and collect reacted particles which have surface films as coatings. The film on the particles may also be
10 used to stabilize materials or may provide a catalytic particle surface for use in subsequent powder metallurgy components, as a sintering aid, or for use as surfactants on particles used in reactor beds.

15 As best shown in Fig. 1, in the reactor 38, the reactive gas 36 is intimately contacted with the molten particles 30 of material 12 in the plasma jet 16. The reactor 38 increases mixing and residence time to allow
20 sufficient contact between the elements 44 and the particles 30 to form the alloyed material 46 (see also Fig. 2). The reactor 38 also allows the particles 30 to remain in a molten state for a longer period of time, thereby enhancing the
25 completeness of the reaction. Preferably, the reactive gas 36 is introduced into the jet sufficiently downstream from the cathode 22 and anode 24 to protect the electrodes from reacting with the reactive gas.

30 It is also preferred that the reactive gas 36 be injected into the reactor 38 as near to the distal end of the nozzle 20 of gun 18 as possible, such as by ring injector 43, in order to prolong the residence time of the particles 30 in

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the reactor 38. Residence times are typically on the order of 20×10^{-3} seconds, although one skilled in the art would understand that the residence time may vary significantly in response to changes in the operating parameters. The preferred concentric, cylindrical shape of the reactor 38 optimizes the mixing process. Addition of the reactive gas 36 in the reactor 38 minimizes any undesirable side reaction between the reactive gas 36 and the cathode 22 and anode 24.

As best shown in Fig. 4, tubular reactor 38 may be cooled by circulating water 56 through cooling jackets 57, although hot wall designs may also be used. To prevent the alloyed material 46 from sticking to the inside of the walls 42 of the reactor 38, a shroud gas 58 may be injected, also by ring injector 43, to flow along the inside of the walls. The shroud gas 58 is preferably an inert gas, such as argon, and may be the same as or different from the inert gas of the plasma jet 16. Typically, the flow rate of shroud gas 58 ranges from 30 to 100 scfh, although this rate may be varied in response to changes in the reactive materials and other processing parameters.

The apparatus 10 further includes means for cooling or solidifying the alloyed material 16. The plasma gun and reactor are preferably attached to and the inert gas stream directed into an environmentally controlled area such as a vacuum chamber 60. Alternatively, the controlled area may be a shroud of inert gas or air in an open environment.

The chamber pressure may range from 1 torr to 760 torr. The chamber 60 may contain an

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inert gas or air, preferably a mixture of argon and helium, i.e. the inert gas of the plasma stream which is continuously exhausted by a vacuum pump (not shown). The inert gas in the chamber 60
5 reduces the likelihood of uncontrolled reactions or contamination of the materials.

The vacuum chamber 60 has a means for mounting a substrate 50 (see Fig. 1) on which to form a deposit or a collector system 64 (see Fig.
10 3) to collect coated particles. The substrate 50 is suitably formed from steel, although one skilled in the art would understand that the substrate 50 may be formed from any high temperature material to be coated in keeping with the spirit and scope of
15 the present invention. The substrate 50 is suitably positioned from 3 to 6 inches from the distal end of the reactor 38. The substrate 50 may be fixed into a robotic manipulator (not shown).

The invention will now be described and
20 illustrated in greater detail by reference to the following specific, non-limiting examples:

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TABLE 1

Run Number	Material	Reactive Gas Type	Reactive Gas Flowrate	Ar Shroud Gas Flowrate
1	C103	Ar	18 scfh	60 scfh
2	C103	N2	35 scfh	70 scfh
3	C103	C3H6	30 scfh	70 scfh
4	C103	C3H6	16 scfh	60 scfh
5	C103	C3H6	16 scfh	40 scfh
6	C103	N2	16 scfh	30 scfh
7	C103	CH4	16 scfh	60 scfh
8	C103	CH4	32 scfh	60 scfh
9	W	Ar	16 scfh	60 scfh
10	W	C3H6	16 scfh	60 scfh
11	W	CH4	16 scfh	60 scfh
12	W	CH4	32 scfh	60 scfh
13	W	CH4	16 scfh	40 scfh
14	W	C3H6	16 scfh	40 scfh
15	Ti	Ar	16 scfh	60 scfh
16	Ti	Ar	16 scfh	60 scfh
17	Ti	Ar	16 scfh	100 scfh
18	Ti	N2	10 scfh	100 scfh
19	Ti	N2	20 scfh	100 scfh
20	Ti	C3H6	10 scfh	100 scfh
21	Ti	C3H6	20 scfh	100 scfh
22	Ti	O2	20 scfh	100 scfh
23	Ti	C3H6+N2+O2	9+9+9 scfh	75 scfh
24	Ti	C3H6+N2+O2	15+15+15+ scfh	75 scfh
25	C103	Si2H6	16 scfh	75 scfh
26	C103	Si2H6	23 scfh	75 scfh
27	FeCrAlY	Ar	20 scfh	75 scfh
28	FeCrAlY	C3H6	10 scfh	75 scfh
29	FeCrAlY	C3H6	20 scfh	75 scfh
30	FeCrAlY	C3H6	10 scfh	75 scfh
31	Mo	Ar	20 scfh	75 scfh
32	Mo	Si2H6	16 scfh	75 scfh
33	Mo	Si2H6	20 scfh	75 scfh
34	Al2O3	Ar+N2	20+24 scfh	75 scfh
35	Al2O3	SiH6+N2	22+24 scfh	75 scfh
36	Al2O3	Ar	20 scfh	75 scfh
37	NiCr+Ti	Ar	20 scfh	75 scfh
38	NiCr+Ti	C3H6	10 scfh	75 scfh
39	NiCr+Ti	C3H6	20 scfh	75 scfh

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TABLE 1 (Continued)

Run Number	Plasma Primary Gas (Ar) Flowrate	Plasma Secondary Gas Type and Flowrate	Spray Distance	VHN (av.)	VHN (av.) load (g)
1	160 scfh	H2, 16 scfh	6 inches	233	500
2	160 scfh	H2, 16 scfh	5 inches	278	500
3	160 scfh	H2, 16 scfh	5 inches	320	500
4	160 scfh	H2, 16 scfh	5 inches	340	500
5	140 scfh	H2, 16 scfh	5 inches	332	500
6	140 scfh	H2, 16 scfh	5 inches	266	500
7	160 scfh	H2, 16 scfh	5 inches	283	500
8	160 scfh	H2, 16 scfh	5 inches	319	500
9	140 scfh	H2, 18 scfh	5 inches	252	500
10	140 scfh	H2, 18 scfh	5 inches	476	500
11	140 scfh	H2, 18 scfh	5 inches	447	500
12	140 scfh	H2, 18 scfh	5 inches	-	500
13	140 scfh	H2, 18 scfh	4 inches	489	500
14	140 scfh	H2, 18 scfh	3 inches	646	500
15	160 scfh	H2, 16 scfh	3 inches	-	300
16	140 scfh	He, 60 scfh	3 inches	-	300
17	140 scfh	He, 60 scfh	3 inches	284	300
18	140 scfh	He, 60 scfh	3 inches	450	300
19	140 scfh	He, 60 scfh	3 inches	525	300
20	140 scfh	He, 60 scfh	3 inches	393	300
21	140 scfh	He, 60 scfh	3 inches	456	300
22	140 scfh	He, 60 scfh	3 inches	693	300
23	140 scfh	He, 60 scfh	3 inches	552	300
24	120 scfh	He, 60 scfh	3 inches	688	300
25	160 scfh	H2, 16 scfh	4 inches	397	500
26	160 scfh	H2, 16 scfh	4 inches	392	500
27	167 scfh	H2, 15 scfh	4 inches	244	300
28	175 scfh	H2, 15 scfh	4 inches	381	300
29	175 scfh	H2, 15 scfh	4 inches	560	300
30	140 scfh	He, 70 scfh	4 inches	385	300
31	160 scfh	H2, 17 scfh	4 inches	308	200
32	160 scfh	H2, 17 scfh	4 inches	491	200
33	160 scfh	H2, 17 scfh	4 inches	546	200
34	140 scfh	H2, 18 scfh	4 inches	-	-
35	140 scfh	H2, 18 scfh	4 inches	-	-
36	140 scfh	H2, 18 scfh	4 inches	-	-
37	140 scfh	He, 70 scfh	4 inches	368	300
38	140 scfh	He, 70 scfh	4 inches	568	300
39	140 scfh	He, 70 scfh	4 inches	838	300

SUBSTITUTE SHEET

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Several gas phase alloying syntheses in accordance with the present invention were run. Table 1 sets forth results for the experiments. The operating parameters and apparatus used were as follows:

The particles 30 are injected at a feed rate of 100 grams per minute. In the present embodiment, the current supplied to the arc is 1100 amperes. In the region of the arc, the velocity of the plasma jet 16 is approximately 1000 m/s. The temperature of the plasma jet 16 upon exiting the gun 18 is approximately 12,000 °K. Upon exiting the reactor, the temperature of the jet 16 is approximately 4000°K to 6000°K.

The present vacuum chamber 60 is similar to that disclosed by A. Ducati in U.S. Patent No. 3,010,009 and that which is commercially available from Electro-Plasma as Model No. LPPS (low pressure plasma spray). The pressure within the chamber 60 is 200 torr.

The substrate 50 is a rectangular steel coupon of 25 mm by 75 mm which is grit blasted with 60 mesh alumina to create a rough surface to facilitate adherence of the alloyed material 46.

Each experimental run was conducted with the following parameters held constant: (1) the chamber pressure was maintained at 200 torr; (2) the plasma arc current was 1100 amps; (3) the material feed rate was 100 g/min with 18 scfh argon as a carrier gas; (4) the spray time was 1 minute.

For example, in Run No. 17, titanium was fed into the plasma jet at a flow rate of 100 g/min. The plasma jet consisted of argon and helium at flow rates of 140 scfh and 60 scfh,

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respectively. As a baseline, argon was used as the gas (non-reactive) at a flow rate of 16 scfh. The argon shroud gas flow rate was 100 scfh. The spray distance was 3 inches. For purposes of comparison, in Run No. 21, titanium was reacted with propylene at a flow rate of 20 scfh. In Run No. 22, titanium was reacted with 20 scfh oxygen. The shroud gas flow rate and spray distance were the same as that used in Run No. 17.

As shown in Table 1, the room temperature microhardness (Vickers hardness number) of the alloyed material formed in Run No. 17, using argon as the "reactive" gas, was 284 VHN (av.) at 300 g load. In contrast, the microhardness of the alloyed material produced in Run No. 21, using propylene as the reactive gas, was 456 VHN (av.), also at a 300 g load. The microhardness value, 693, when oxygen was used as the reactive gas (Run No. 22) was almost double the value obtained when argon was used.

The advantages of the present method in increasing the hardness of a material is shown by the results of Runs 31 and 33, which use molybdenum as the material to be alloyed. Since molybdenum has a higher melting point than titanium, a plasma jet consisting of 160 scfh argon and 17 scfh hydrogen was used to facilitate the reaction. For both runs, the argon shroud gas flow rate was 75 scfh and the spray distance was 4 inches. In Run No. 31, the "reactive gas" was argon at a flow rate of 20 scfh. For purposes of comparison, in Run No. 33, molybdenum was reacted with disilane, also at a flow rate of 20 scfh.

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As set forth in Table, the microhardness of the alloyed material formed in Run No. 31, using argon as the reactive gas was 308 VHN (av.) at 200 g load. The microhardness of the alloyed material
5 produced in Run No. 33, using disilane as the reactive gas, was 546 VHN (av.), also at a 200 g load. Similarly dramatic results were observed for other test materials.

It will be appreciated by those skilled
10 in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed,
15 but it is intended to cover modifications which are within the spirit and scope of the invention as defined by the appended claims.

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CLAIMS

1. A method for gas phase diffusion alloying of a material selected from the group consisting of metals and ceramics, comprising the
5 steps of providing a high temperature stream of inert gas, injecting solid particles of said material into said stream, the temperature of said stream being sufficient to substantially liquefy said particles, injecting a reactive gas into said
10 stream for dissociation in the high temperature stream and reaction with said particles while said particles are suspended in said stream and are at least partially in a liquid state, whereby at least one dissociated element of said reactive gas
15 diffuses into said liquid particle to form a compound of said material and said element in at least a portion of said particle, and cooling the thus alloyed material.

2. A method according to claim 1,
20 wherein said high temperature stream is a plasma jet.

3. A method according to claim 2, wherein said jet propels the alloyed material against a substrate, whereby said particles rupture
25 and produce on the substrate surface a deposit comprising dispersoids of said compound in said material.

4. A method according to claim 1, wherein said alloyed material is cooled and
30 collected as a coated particle.

5. A method according to claim 4, wherein said coating comprises said compound.

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6. A method according to claim 1, wherein said element is selected from the group consisting of C, N, O, Si, B, H, S, F, Cl.

7. A method according to claim 1,
5 wherein said reactive gas is injected into said stream after said stream is heated to said high temperature, the reactive gas being injected upstream, downstream, or at the point of injection of said particles into said stream.

10 8. A method according to claim 1, wherein said reactive gas is injected into said stream downstream from injection of said particles into said stream.

15 9. A method according to claim 1, wherein said inert gas is heated by a direct current arc or a radio frequency induction coupled discharge.

20 10. A method according to claim 1, wherein said inert gas is selected from the group consisting of argon, helium, hydrogen, nitrogen, and combinations thereof.

25 11. A method according to claim 1, wherein said material is selected from the group consisting of transition metals, aluminum, silicon, and combinations and oxides thereof.

30 12. An apparatus for high temperature gas phase diffusion alloying of an element of a reactive gas with a material selected from the group consisting of metals and ceramics, comprising means for supplying a stream of inert gas, means for heating said gas to a temperature sufficient to liquefy particles of said material and to dissociate said reactive gas, means for injecting solid particles of said material into said heated

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stream, means for injecting a reactive gas containing said element into said heated stream, said particle-injecting means and said reactive gas-injecting means being positioned relative to
5 said heated stream so that said reactive gas will not react with said heating means but will dissociate said reactive gas for diffusion of said element into said particle while said particles are at least partially in a liquid state, and means for
10 cooling the alloyed material.

13. An apparatus according to claim 12, wherein said means for supplying and heating said inert gas stream comprises a plasma gun.

14. An apparatus according to claim 13,
15 wherein said plasma gun is equipped with a gas spray nozzle for accelerating said heated stream and said particle-injecting means comprises inlet ports adjacent the upstream end of said nozzle.

15. An apparatus according to claim 12,
20 wherein said plasma gun is equipped with a tubular reactor having an inlet port in its wall, said inlet port comprising said reactive gas-injecting means.

16. An apparatus according to claim 15,
25 further including means for providing a shroud gas along the inside walls of said reactor, whereby said shroud gas inhibits materials from depositing on said reactor wall.

17. An apparatus according to claim 12,
30 wherein said plasma gun is attached to and its inert gas stream is directed into a controlled area having collection means for receiving a spray of said alloyed material.

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18. An apparatus according to claim 17,
wherein said controlled area comprises a vacuum
chamber.

19. An apparatus according to claim 17,
5 wherein said collection means comprises a collector
system for collecting coated particles.

20. An apparatus according to claim 17,
wherein said collection means comprises a substrate
to be coated with said alloyed material.

10 21. An apparatus according to claim 12,
wherein said heating means is selected from the
group consisting of a direct current arc and a
radio frequency induction coupled gas heater.

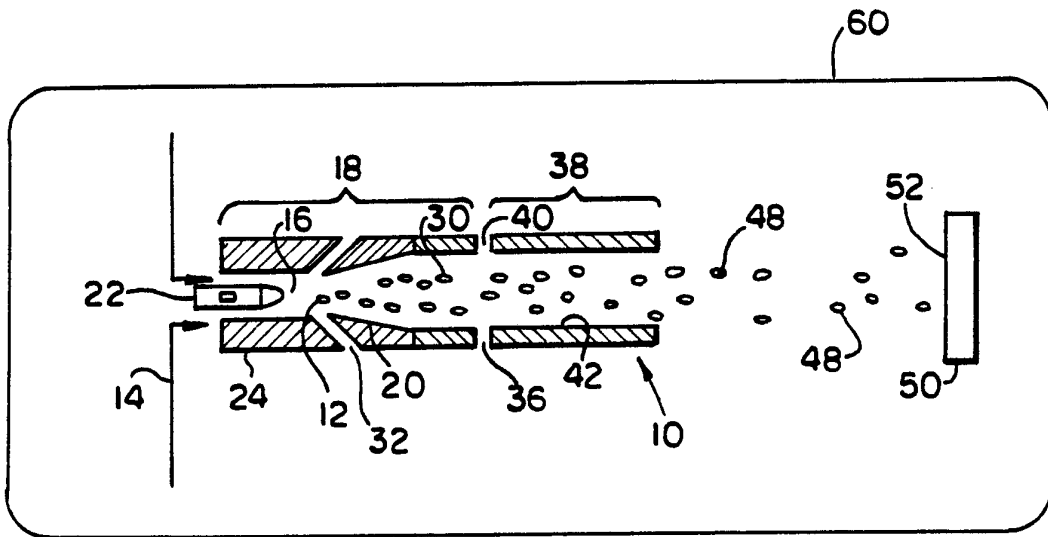


FIG. 1

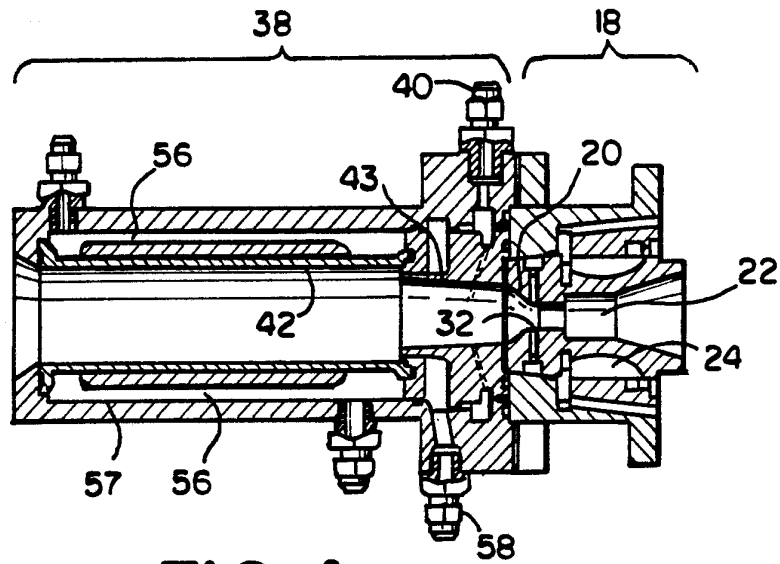


FIG. 4

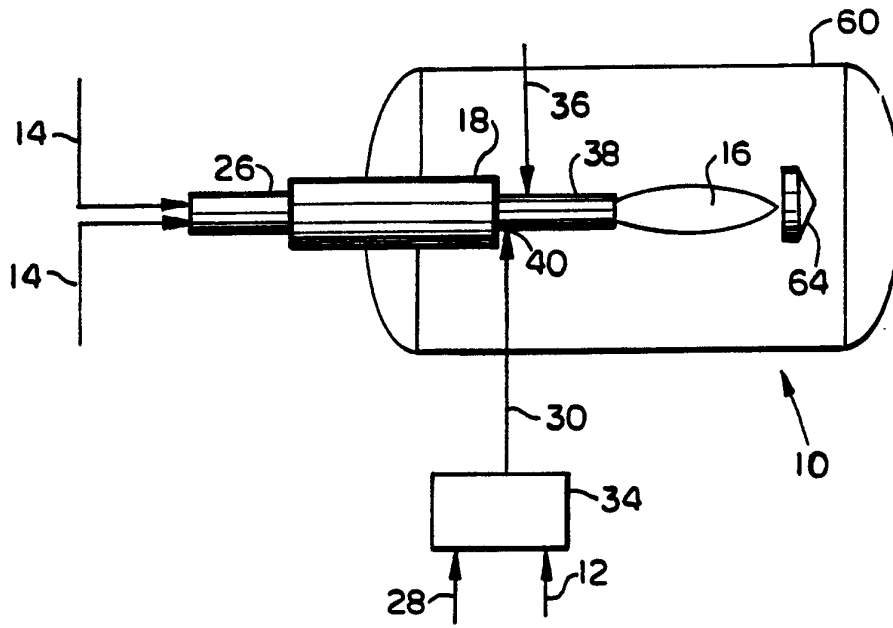


FIG. 3

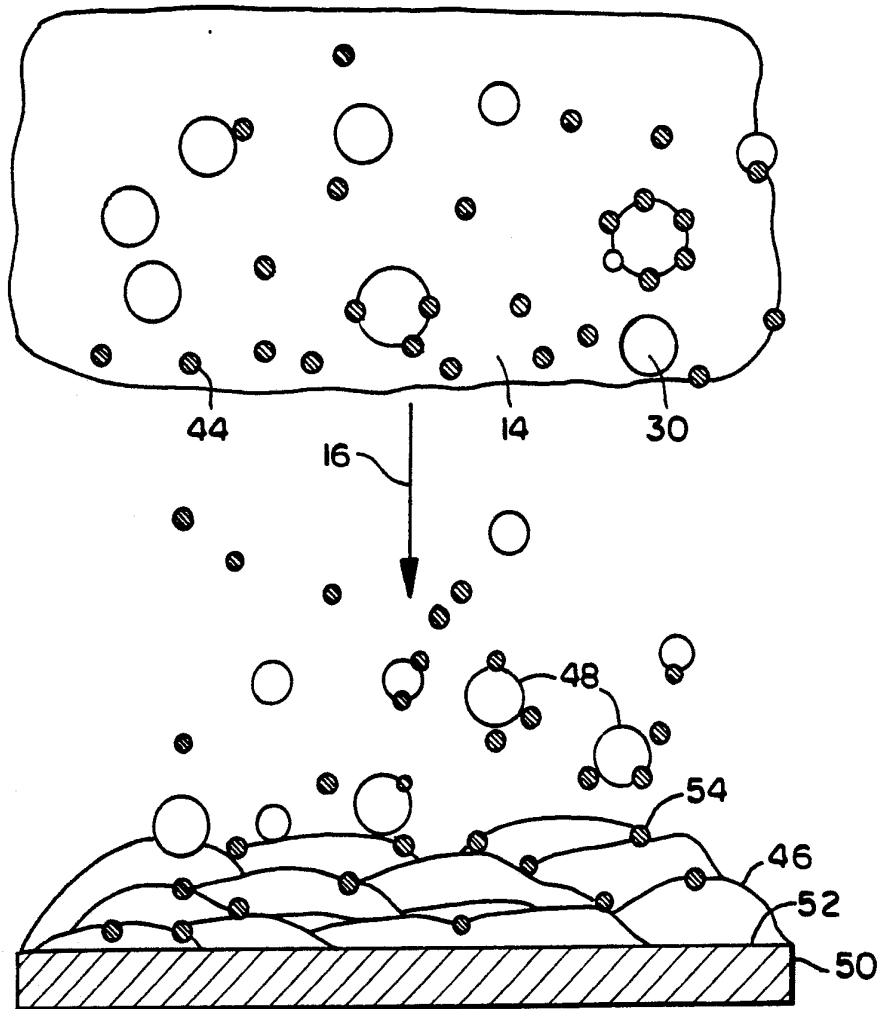


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US92/01132

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC(5) C23C 26/00		
U.S. CL. 420/590		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	75/346, 351, 352, 332, 360, 334; 118/620, 723 219/121.47; 264/5-10, 12, 14; 420/490; 425/6,7 427/34, 255.1, 255.2	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	US, A, 4,778,515 (Kemp et al) 18 October 1988 (claim 1).	1-11
Y	US, A, 3,909,241 (Cheney et al) 30 September 1975 (col. 1 lines 64- col. 2 line 45)	1-21
Y	GB, A, 1,141,775 29 January 1969 (page 1, lines 27-34 and 41-45)	1-21
Y, P	US, A, 5,043,548 (Whitney et al) 27 August 1991 (claims 1-6)	12-21
Y	US, A, 4,898,748 (Kruger, Jr) 06 February 1990 (claims 1-16)	12-21
Y	US, A, 4,741,286 (Itoh et al) 03 May 1988 (abstract)	12-21
Y	US, A, 4,731,517 (Cheney) 15 March 1988 (claims 1-26)	12-21
Y	US, A, 4,818,837 (Pfender) 04 April 1989 (col. 6 lines 4-35 & claims 1-10)	12-21
<p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
11 May 1992		18 JUN 1992
International Searching Authority		Signature of Authorized Officer
ISA/US		Sikyin Ip <i>Sikyin Ip</i>

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. Claim numbers _____ because they relate to subject matter ¹² not required to be searched by this Authority, namely:

2. Claim numbers _____ because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. Claim numbers _____ because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ²

This International Searching Authority found multiple inventions in this international application as follows:

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- The additional search fees were accompanied by applicant's protest.
 No protest accompanied the payment of additional search fees.