



(51) International Patent Classification:

C23C 16/06 (2006.01) C22B 34/12 (2006.01)
C23C 16/513 (2006.01) H05H 1/42 (2006.01)
B05B 7/22 (2006.01) H01J 37/32 (2006.01)
C23C 4/12 (2006.01)

(21) International Application Number:

PCT/EP2012/056798

(22) International Filing Date:

13 April 2012 (13.04.2012)

(25) Filing Language:

English

(26) Publication Language:

English

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD,
SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR,
TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU,

[Continued on next page]

(54) Title: METHOD AND SYSTEM FOR PRODUCTION AND ADDITIVE MANUFACTURING OF METALS AND ALLOYS

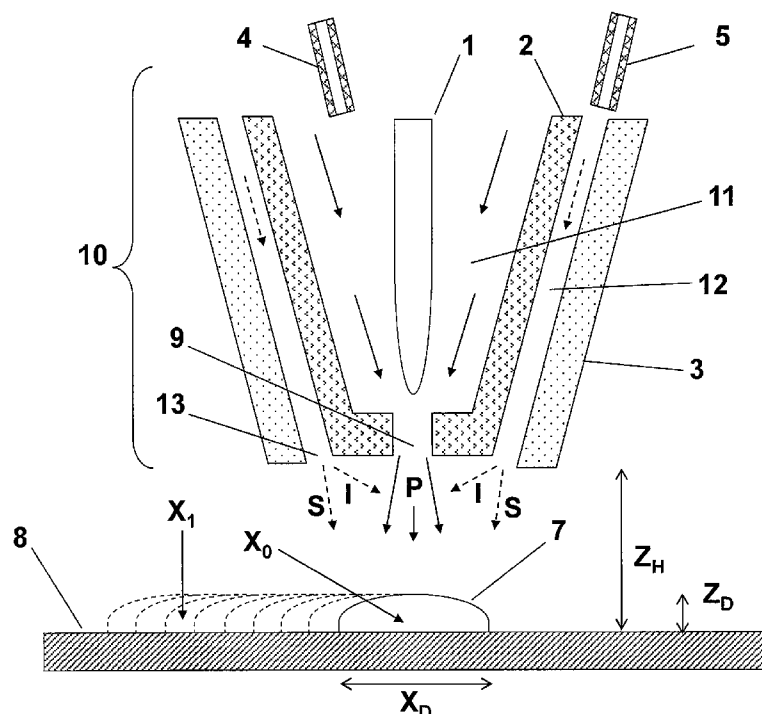


FIG. 1

(57) Abstract: A method and system are disclosed for depositing materials comprising metals and alloys by decomposing one or more metal iodides using a directed plasma arc source. Additive manufacturing of shaped components may be accomplished by directing the source output towards defined regions of a work-piece.



TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

METHOD AND SYSTEM FOR PRODUCTION AND ADDITIVE MANUFACTURING OF METALS AND ALLOYS

TECHNICAL FIELD

The invention relates to the production and additive manufacturing of metals and alloys using plasma sources.

BACKGROUND

Many conventional metallurgical processes cannot be used with metals that have a high affinity for oxygen at elevated temperatures, greatly increasing the costs of producing such metals and their alloys. For example, Ti alloys, despite properties generally far superior to steels and aluminum alloys, notably high specific strength and excellent corrosion resistance, are too expensive for high volume applications, Zr alloys, despite offering excellent corrosion resistance, hardness and ductility, are largely confined to nuclear applications, where their low cross section for thermal neutrons is invaluable, and Be alloys, despite offering a high specific strength and extremely low density, setting aside the toxicity of certain Be compounds, are too expensive for all but specialized aerospace and nuclear applications.

Commercial quantities of Zr and Ti having acceptably low levels of oxygen were first produced by the Van Arkel process, developed in the 1920s, in which metal iodide vapor is decomposed upon contact with an incandescent surface, typically a wire or plate held around 1500 K, to leave a deposit of pure metal. See US Pat. No. 1,671,213 (Philips). Iodide vapor may be formed by heating the metal iodide (TiI_4 and ZrI_4 , for example, are volatile solids at room temperature) or exposing the metal, heated to an

intermediate temperature, to iodine vapor. Though originally proposed for Ti, Zr, Hf and Th only, the Van Arkel process can, in principle, be used with any metal iodide amenable to thermal decomposition in its vapor phase. However, early investigators deemed the production of Be from solid BeI_2 unfeasible, in view of unfavorable reaction kinetics at the melting point of Be. See R.S. Babu & C.K. Gupta, *Beryllium Extraction—A Review*, 4 Min. Proc. & Extract. Met. 39, 74 (1988). Indeed, even with more favorable kinetics, the conventional Van Arkel process is inherently slow, and therefore uneconomical for all but niche applications which require relatively small amounts of extremely pure metal.

Most Ti and Zr metal is now produced using the more economically viable Kroll process, in which metal tetrachloride is reduced with batches of molten Mg to form metal sponge intermixed with MgCl_2 and unreacted Mg. Alloys of Ti and Zr are nevertheless still expensive. For example, even though liquid TiCl_4 costs only a few Euros per kg, the combined costs of producing Ti sponge and processing leave a standard Ti-6Al-4V alloy ingot costing a few tens of Euros per kg. Further, traditional manufacturing techniques—such as casting, forging or machining—tend to consume significantly more alloy than is actually required in a finished component, adding to the cost of components made from alloys of metals, such as Ti, Zr and Be, already rendered expensive by their high affinity for oxygen at elevated temperatures.

In light of these cost concerns, a range of manufacturing technologies—variously aimed at consuming less material, using less expensive starting materials, and reducing the number, duration and cost of processing steps—have been proposed and developed, particularly for Ti alloy components. Among these, additive manufacturing

technologies employ a localized heat source—typically an electron beam, laser or plasma arc—to heat and melt feedstock—typically in the form of wire or powder—as it is applied in successive layers to well-defined regions of a work-piece to create a finished, or nearly finished, three-dimensional shaped component. For example, US Pat. App. No. 2006/0185473 (Mats. & Electrochem. Res. Corp.), proposes additive manufacturing of shaped titanium components using a maneuverable plasma transferred arc (“PTA”) welding torch directed towards a work-piece, coupled with means for feeding Ti sponge/ceramic particles into the torch and Ti/Ti alloy wire into the melt pool formed at the surface of the work-piece by the torch output.

However, for many additive manufacturing technologies, the cost savings arising from the consumption of less metal per finished component and fewer processing steps are offset by the greater cost of the powder or wire starting material. For example, a standard Ti alloy powder or wire made from Kroll process Ti can cost of the order of a few hundred Euros per kg. Efforts to reduce the high cost of starting materials have included development of a continuous process for producing Ti-based powders by bubbling TiCl_2 gas through molten sodium. W.H. Peter et al., *Non-Melt Processing of “Low Cost”, Armstrong Titanium and Titanium Alloy Powders*, Proc. 3rd Int’l Light Metals Tech. Conf. (Saint-Sauveur-des-Monts, 2007); US Pub. Pat. App’n. 2006107790 (Int’l Titanium Powder, LLC). Other efforts have aimed at dispensing with expensive starting materials, including a proposal for reactive plasma spray manufacture of TiAl coatings and components using TiCl_4 gas in a plasma welding torch and a stream of Al powder. US Pat. No. 5,217,747 (Noranda, Inc.).

Despite the availability of inexpensive metal iodides (which can be formed, for example, by reacting inexpensive metal chloride and HI), a viable high-volume iodide route for production and additive manufacturing of metals and alloys has yet to be developed. Proposals have included a vacuum chamber housing an ionized metal iodide molecular jet impinging on a charged metal plate, GB Pat. No. 792,638 (Nat'l. Res. Dev. Corp.), or an arc formed in a metal iodide vapor stream flowing between a carbon electrode and a melt pool on the surface of a charged metal ingot, US Pat. No. 2,768,074 (Nat'l. Res. Corp.). Efforts to apply laboratory scale plasma sources—magnetron, coaxial line resonator and induction—to the decomposition of metal halides, including chlorides of Ti and Be in the presence of H₂, were not attempted with iodides. See US Pat. No. 3,533,777 (CSIRO). Other attempts to form Ti powder, by injecting liquid or vapor phase TiI₄ into a non-PTA source, yielded a mixture of Ti-I phases, notwithstanding predictions of a high proportion of isolated Ti at the anticipated plasma operating temperatures and pressures. F.K. Ojebuoboh, *An Assessment of Titanium Metal Production in a Plasma Reactor by TiI₄ Disproportionation*, Ph.D. thesis, Colorado School of Mines (1985); F.K. Ojebuoboh & G.P. Martins, *High-Temperature Equilibria in the Disproportionation of Titanium Tetraiodide*, 24 High. Temp. Sci. 71 (1987).

More recently, TiI₄ has been used successfully, in combination with H₂ and other gases, in plasma chemical vapor deposition ("PCVD") to form the extremely thin Ti and Ti₃N₄ films used in microelectronics. See, e.g., US Pat. No. 7,033,939 (Micron Techs., Inc.).

The present invention overcomes the above and other limitations of the prior art by enabling production of metals and alloys in bulk and powder form, and additive

manufacturing of metal alloy components, using metal iodides in a directed plasma system.

SUMMARY OF THE INVENTION

A method is disclosed for forming a material comprising a first metal, comprising the
5 steps of furnishing a plasma head comprising a plasma generation volume, establishing
a first flow comprising an inert gas traversing the plasma generation volume and
plasma head, applying a plasma voltage across the plasma generation volume to
establish a plasma arc comprising an internal portion confined within the plasma head,
establishing a second flow comprising a first metal iodide configured to combine with
10 the first flow and traverse at least a portion of the plasma arc, regulating the first and
second flows and plasma power to fully decompose at least a substantial fraction of
the first metal iodide in the combined flow, directing at least a fraction of the
combined flow comprising the at least a substantial fraction of fully decomposed first
metal iodide to contact a region of a surface of the work-piece, and depositing a
15 material comprising the first metal on at least a fraction of the region.

In other embodiments, the method further comprises forming an external portion of
the plasma arc extending outside the plasma head, optionally contacting at least a
fraction of the region with the external portion of the plasma arc and optionally
establishing a transfer voltage between the work-piece and plasma head to form a
20 transferred plasma arc.

In other embodiments, the method further comprises combining the second flow
comprising the first metal iodide with the first flow before the first flow exits the

plasma generation volume, before the first flow exits the plasma head, or in the external portion of the plasma arc.

In another embodiment, the method further comprises establishing a third flow comprising a second metal iodide configured to combine with the first flow and
5 traverse at least a portion of the plasma arc, regulating the first, second and third flows and plasma power to fully decompose at least a substantial fraction of the first and second metal iodides in the combined flow, directing at least a fraction of the combined flow comprising the at least a substantial fraction of fully decomposed first and second metal iodides to contact a region of a surface of the work-piece, and
10 depositing a material comprising an alloy of the first and second metals on at least a fraction of the region.

In other embodiments, the method further comprises combining the third flow comprising the second metal iodide with the first flow before the first flow exits the plasma generation volume, before the first flow exits the plasma head, or in the
15 external portion of the plasma arc.

In another embodiment, the method further comprises establishing a fourth flow comprising a third metal iodide configured to combine with the first flow and traverse at least a portion of the plasma arc, regulating the first, second, third and fourth flows and plasma power to fully decompose at least a substantial fraction of the first, second
20 and third metal iodides in the combined flow, directing at least a fraction of the combined flow comprising the at least a substantial fraction of fully decomposed first, second and third metal iodides to contact a region of a surface of the work-piece. And

depositing a material comprising an alloy of the first, second and third metals on at least a fraction of the region.

In other embodiments, the method further comprises combining the fourth flow comprising the third metal iodide with the first flow before the first flow exits the plasma generation volume, before the first flow exits the plasma head, or in the external portion of the plasma arc.

In yet other embodiments, the method further comprises at least one of the metal iodide flows comprising at least a substantial fraction of metal iodide in a solid, liquid or gas phase when it combines with the first flow.

In some embodiments, the first metal iodide is selected from the group consisting of TiI_4 , ZrI_4 or BeI_2 , and the second and third metal iodides from the group consisting of VI_3 , AlI_3 , ZrI_4 , BeI_2 , HfI_4 , NbI_3 , TaI_3 , BiI_3 , SiI_4 , SbI_3 , GdI_3 , NdI_3 , ThI_4 , MoI_2 , CoI_2 , NiI_2 , MgI_2 , SnI_4 and Cl_4 .

In other embodiments, the method further comprises delivering microwave energy into the at least a portion of the combined flow at a frequency spectrum and power selected to break apart at least one metal-iodine species

In yet other embodiments, the method further comprises introducing a seeding material into the combined flow to condense clusters comprising the one or more metals in the at least a fraction of the combined flow comprising at least a substantial fraction of the one or more fully decomposed metal iodides. The seeding material may traverse at least a portion of the internal or external or no portion of the plasma arc, and may comprise metal particles, selected, for example, from the group consisting of

Al, V, Si, B, Mo, Be and Ti, or ceramic particles, selected, for example, from the group consisting of TiB_2 , SiC , WC , BN , Y_2O_3 and ZrO_2 .

In some embodiments, the at least a portion of the fraction of the combined flow contacting the region further may comprise hydrogen or one or more of the first,
5 second, third or fourth flows may further comprise hydrogen.

In some embodiments, the deposited material is deposited in a molten state and in others in a solid state. In other embodiments, an additional heat source is applied to the deposited material.

In yet other embodiments, a controlled relative motion of plasma head and work-piece
10 is applied to form successive layers of deposited material in different regions of the work-piece to create a shaped component.

In still yet other embodiments, the flow from the outlet to the work-piece is surrounded with an inert gas shield, and the work-piece and plasma head are furnished in a vacuum chamber.

15 In yet other embodiments, a system is provided for implementing any of the above methods, wherein the plasma generation volume is defined by an outer surface of an elongated cathode and an inner surface of a coaxially disposed anode, and wherein the first flow comprising an inert gas passes through a first opening formed in a lower surface of the plasma head.

20 In other embodiments, the plasma head further comprises a substantially coaxial shield and a substantially annular opening disposed coaxially in the lower surface of the plasma head with respect to the first opening, and wherein an axially symmetric

volume is defined by an outer surface of the anode and an inner surface of the shield and configured to deliver a gas flow from an upper portion of the plasma head through the annular opening.

In yet other embodiments, the flow from the annular opening is configured to be substantially parallel with and enclose the flow from the first opening, intersect the flow from the first opening or intersect the external portion of the plasma arc.

In still other embodiments, the plasma head comprises a feeder for directing a flow of at least one metal iodide into the coaxial volume, into the plasma generation volume, or into the flow between the plasma head and work-piece.

In other embodiments, the system further comprises one or more of an induction source disposed to deliver microwave energy to the combined flow from the plasma head, a means for delivering at least one additional material directly to the deposited material on the region, a heat source configured to deliver heat directly to the deposited material on the region, control mechanisms for translating the work-piece and the plasma head, a vacuum-pumped chamber housing the work-piece and plasma head and a means for condensing iodine disposed in the vacuum chamber.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a schematic of part of a plasma system illustrating features of the invention.

Figure 2 is a schematic of part of a plasma system illustrating features of the invention.

Various features of the invention are described herein with reference to the figures, the written description and claims. These features may be combined with or interchanged in any permutation other than one in which the features are mutually

exclusive. Comprising is used to mean including but not limited to. Confined is used to mean within but not necessarily filling a defined volume or space. Combined is used to mean substantially but not necessarily completed united or joined. Work-piece and work-piece surface are used to refer to the object and surface onto which deposition is performed, which may include a substrate, not necessarily comprising the metal or alloy being deposited, and may include already deposited metal or alloy material, including a portion of a metal or alloy component.

DETAILED DESCRIPTION

Different plasma sources may be configured to establish a plasma arc in a flow comprising an inert gas that may be combined with a flow of one or metal iodides to form a directed combined flow comprising one or more metals formed by decomposition of the metal iodide or iodides, suitable for depositing a material comprising a metal or alloy on a work-piece.

An example of a suitable plasma source, shown in Figures 1 and 2, is a plasma head **10**, of a type commonly referred to as a plasma torch when operated to produce an external plasma arc. Plasma head **10** comprises an axially disposed cathode **1** partially enclosed by a more-or-less axially symmetrical hollow anode **2**, with the space between the outer surface of cathode **1** and the inner surface of anode **2** defining a plasma generation volume **11** adapted to accommodate a first flow, shown schematically in Figure 1 by the arrows contained within coaxial volume **11**, comprising an inert gas, typically argon, that enters the upper portion of the head through an inlet (not shown) and exits the plasma generation volume, and optionally the plasma head **10**, through opening **9**, which is typically axially symmetric and disposed in the base of

anode **2** aligned with axis of cathode **1**. (Required electrical connections and the upper portions of cathode **1**, anode **2** and plasma generation volume **11** are not shown.)

A plasma arc may be generated within plasma generation volume **11** by applying an appropriate high voltage (of the order of 10 kV) between cathode **1** and anode **2** across

5 the first flow comprising an inert gas. By regulating the first flow, namely by regulating the composition, mass flow and/or inlet pressure, and by regulating the plasma power, typically between 1 and 10 kW, namely by regulating the plasma voltage and current, a

range of plasma arc configurations may be established for a given plasma head geometry. An internal portion of the plasma arc, with a defined temperature and

10 pressure distribution and spatial extent confined within the plasma head, may be

established in at least part of the plasma generation volume **11**, and an optional external portion of the plasma arc, with a defined temperature and pressure distribution and spatial extent extending at least some way through opening **9**, may be established outside the head. In particular, by virtue of the flow constriction imposed

15 by opening **9**, plasma arc temperature and pressure may be substantially increased.

Typically, in the majority of the internal and external portions of the plasma arc, pressure may vary between around 0.1 to around 100 kPa and temperature, between around 3000 to around 5000 K, with the diameter of the opening **9** in the base of the plasma head **10** typically varying from around a few 100 microns to around a few cm.

20 (Though not shown in the figures, anode **2** may be cooled by internal water flow.)

The pressure and temperature distribution and spatial extent of the external portion of the plasma arc may be further influenced by factors such as external gas flows, the relative location of the work-piece, and the presence of a transfer voltage between

work-piece and plasma head that induces the external plasma arc to contact the work-piece surface **8**, forming a so-called plasma-transferred-arc (“PTA”). In general, a PTA may be more directed than a non-PTA and a more efficient means to transfer heat energy to material deposited on the work-piece.

- 5 As shown in Figures 1 and 2, plasma head **10** may further comprise a more-or-less axially symmetrical element **3** partially enclosing anode **2**, with the space between anode **2** and element **3** defining a coaxial volume **12** adapted to accommodate a flow, shown schematically by the dashed arrows contained within coaxial volume **12** in Figure 1, between the upper portion of the head and a more-or-less annular opening
10 **13** defined by the lower end of element **3** and the outer surface of anode **2**. The flow, typically comprising an inert gas, traversing coaxial volume **12** may also serve to cool anode **2**.

- In some embodiments, the lower end of element **3** and outer surface of anode **2** may be adapted to direct the flow from opening **13** on an inwardly sloping inclined path
15 intersecting the first flow exiting opening **9**, as shown by inclined dashed arrows **I**. The flow exiting through annular opening **13** may be used to combine material into the external portion of plasma arc **P** extending beyond opening **9**. The proximity of the outer surface of anode **2** may allow material in this second flow to be heated before combination with the first flow. (Though not shown, element **3** may be adapted to at
20 least partially cover the lower surface of anode **2**, such that the lower surface of element **3** becomes the lower surface of plasma head **10** and the second flow combines with the first flow before it exits plasma head **10**.)

In other embodiments, the lower end of element **3** and outer surface of anode **2** may be adapted to direct the flow from annular opening **13** to be more-or-less parallel to the flow exiting opening **9**. Such an inert gas may be used to form a shield around the plasma arc exiting opening **9** and those regions of the work-piece surface **8** or deposited material **7** heated by the plasma arc. The shield flow is indicated by dashed arrows **5** in Figures 1 and 2. (Where the flow from opening **13** is directed into a plasma arc exiting orifice **9**, as shown by dashed arrows **1**, a second element may be adapted to provide an inert gas shield for the plasma arc exiting opening **9** and flow exiting opening **13**.)

Using the plasma source shown in Figures 1 and 2, a range of operating conditions may be established to achieve full decomposition of at least a substantial fraction of one or more metal iodide flows, by appropriately configuring the temperature and pressure within those portions of the plasma arc traversed by the one or more metal iodide flows, the dwell time of the one or more metal iodide flows within traversed portions of the plasma arc, and the relative proportions of the mass flows of metal iodide and inert gas.

Various configurations of one or more flows comprising metal iodides or inert gas may be established using the system shown in Figures 1 and 2. For example, Figure 1 shows material feeder **4**, positioned to establish a flow comprising a metal iodide that combines with the first flow comprising an inert gas before the first flow has entered or completely traversed plasma generation volume **11**. Such a configuration may allow a metal iodide flow to traverse a maximum portion of the plasma arc. (A suitable material feeder may include a means for directing a stream of powder, liquid or gas,

possibly premixed with a gas or other gas, and possibly preheated.) On the other hand, material feeder **5** is shown positioned to introduce a flow comprising a metal iodide that passes through coaxial volume **12**, exits opening **13** and, as shown schematically by dashed arrows **I**, combines with the first flow after the first flow has exited both plasma generation volume **11** and plasma head **10** to form external plasma arc **P**. (Were element **3** to at least partially cover anode **2**, and therefore define the outer boundary of the plasma head, a configuration not shown in Figures 1 or 2, the second flow might combine with the first flow after the first flow had exited the plasma generation volume **11**, but before it had exited plasma head **10** to form external plasma arc **P**.) By suitably configuring the spatial extent, temperature and pressure distribution of the external portion of the plasma arc **P**, and the relative composition, mass flow and velocity profile of the flow exiting opening **13**, at least a substantial fraction of the metal iodide flow originating with feeder mechanism **4** may be fully dissociated in the combined flow exiting plasma head **10**.

Though Figure 1 shows only two asymmetrically placed material feeders **4** and **5**, fewer or more may be used, and they may be placed symmetrically with respect to the plasma head. One or more flows comprising different metal iodide may be established using one or more material feeders disposed as feeders **4** or **5**. More than one metal iodide may be introduced in the same feeder to establish a combined flow of one or more metal iodides. The same metal iodide may be introduced using more than one feeder.

Figure 2 also shows material feeder **15** external to the plasma head and positioned to combine a second flow comprising a metal iodide with the first flow in the external

plasma arc **P**. (Were a PTA established, material feeder **14** shown in Figure 2 would also be positioned to combine a second flow comprising a first metal iodide with the first flow in the external plasma arc **P**.) Though Figure 2 shows only two asymmetrically placed material feeders **14** and **15**, fewer or more may be used, and these may be placed symmetrically with respect to the axis of the plasma head. One or more metal iodide flows comprising one or more metal iodides may be established using one or more material feeders disposed as feeders **14** or **15**. More than one metal iodide may be introduced in the same feeder to establish a combined flow of one or more metal iodides. The same metal iodide may be introduced using more than one feeder.

Suitable metal iodide or iodides may be stored in solid form, for example, as powder in a hopper, or in the form of a liquid or gas. A supply of metal iodide may also be produced, as needed, by a suitable chemical process. (For example, TiI_4 may be formed by reacting $TiCl_2$ with HI , or Ti with I_2 vapor.) A metal iodide flow comprising metal iodide substantially in a solid, liquid or gaseous state may be combined into the first flow. For example, a flow comprising a solid metal iodide in powder form, introduced using material feeder **4** shown in figure 1, may be heated as it passes through coaxial volume **12**, to form liquid or gas phase metal iodide before combination with the first flow, or the metal iodide may be preheated to form liquid or vapor before it is introduced from feeder mechanism **4**.

Feeder mechanisms such as those indicated as **4**, **5**, **14** and **15** may be used with materials other than metal iodides. For example, a flow comprising particles of a seeding material, as described below, or metals that do not form suitable iodide

compounds, may be introduced. Gases other than inert gases, including hydrogen, as also described below, may also be introduced with such feeder mechanisms.

As also shown in Figure 2, an optional microwave source **18**, typically an induction system operating at around a few GHz, may be used to deliver additional energy to the plasma stream or flow **P** or gas stream or flow **G** exiting the plasma head **10**. (Plasma **P**, as opposed to gas **G**, is shown passing through source **18**.) The power and frequency spectrum delivered by source **18** may be tuned to transmit energy to one or more specific metal-iodine bonds, in an effort to break apart residual non-decomposed metal iodide species.

By directing at least a fraction of the combined flow from the plasma head comprising at least a substantial fraction of fully decomposed metal iodide or iodides to contact a region of a surface of the work-piece, a deposited material **7** comprising one or more metals may be formed on at least a fraction of the region **8**. The temperature of the deposited material **7** may be adjusted, for example, by varying the power and extent of the external plasma arc and the work-piece to plasma head distance, to ensure formation of a fully molten metallic deposit, or to suppress back reaction of solid or liquid metallic material with iodine. A reducing gas, such as hydrogen, may also be introduced, optionally as part of the combined flow or with any of the metal iodide or other material flows, to react with the free iodine released by the decomposition of metal iodides or with residual any metal iodides.

Additional material, generally not comprising a metal iodide, may be combined into the heated or molten material **7** formed on work-piece surface **8**. Feeder mechanism **16** shown in the figure may be, for example, a powder feeder or a wire feeder of

known type. An additional heat source, such as a laser, may also be used to increase the temperature of material deposit, and optionally apply heat to the additional material from a source such as feeder **16**.

The metal species formed by decomposition of one or more metal iodides in the plasma arc may be induced to condense to form solid or liquid clusters before coming into contact with the work-piece. In order to facilitate such condensation, a seeding material that promotes heterogeneous nucleation of metal clusters may be introduced into the combined flow. For example, an appropriate seeding material may be introduced using means **4** shown in Figure 1 leading, through volume **12**, into the inclined directed annular flow **I**, or using an introduction means external to the plasma head and directed towards external portion of the plasma arc **P**, shown as introduction means **15** in Figure 2, or directed towards gas flow **G**, shown as introduction means **14** in Figure 2. Suitable materials that may be used for seeding cluster condensation in metals, such as Ti, Zr and Be, include metal particles, such as Al, V, Si, B, Mo, Be and Ti, and ceramic clusters, such as TiB₂, SiC, WC, BN, Y₂O₃, ZrO₂. Seeding materials may be used in alloy deposition, for example, with Ti, Zr and Be alloys. The size distribution of seeding material particles may be optimized to ease handling and introduction into the combined flow, while providing a suitable density of nuclei.

By using different combinations and proportions of one or more metal iodide flows, different combinations of metals and alloys may be deposited at different rates and at different times on the work-piece. For example, by employing solely or mainly TiI₄ in one more metal iodide flows, Ti metal or alloys may be deposited, and by employing solely or mainly ZrI₄ or BeI₂, Zr or Be metals or alloys may be deposited. As a means of

depositing an alloy material onto the work-piece, the primary metal iodide may be pre-mixed with defined amounts of more than one other iodide before introduction of the mixture into the plasma system using one or more feeder mechanisms.

As an alternative means for depositing an alloy material, more than one metal iodide
5 may be introduced simultaneously into the plasma system using separate feeder mechanisms. When the physical properties of various metal iodides are substantially different, it may be necessary or desirable to use separate feeder mechanisms, and possibly iodides in different physical states, optimized to ensure the full decomposition of each iodide species. For example, the feeder for the flow comprising BeI_2 , an iodide
10 for which the kinetics may be less favorable, may be configured to traverse a greater portion of the plasma arc and combine with the plasma arc with the iodide already vaporized, while the feeder for TiI_4 , may be configured to be traverse a smaller portion of the plasma arc and combine with the iodide still in a solid phase.

Suitable iodides for producing alloys include Vl_3 , AlI_3 , ZrI_4 , BeI_2 , HfI_4 , NbI_3 , TaI_3 , BI_3 , SiI_4 ,
15 SmI_2 , GdI_3 , NdI_3 , ThI_4 , MoI_2 , CoI_2 , NiI_2 , MgI_2 , SnI_4 and Cl_4 . As an example of alloy production, where the primary metal iodide flow is TiI_4 , appropriate flows of Vl_3 and AlI_3 (adjusted to take account of any V and Al introduced as seeding material), may be configured to deposit a Ti-6Al-4V alloy on the work-piece. As noted above, one or more of these metal iodides may be premixed and introduced using the same feeder
20 or feeder mechanisms, or may be introduced in separate flows. Suitable combinations of metal iodide flows may also be used to deposit alloys of Zr and Be, with ZrI_4 or BeI_2 , respectively, comprising the first metal iodide flow, in place of TiI_4 , and with suitable

alloying components being introduced as one or more other metal iodide flows, including iodides selected from the group listed above.

Depending on the required total deposition rate, plasma sources may be furnished in a range of sizes and operating powers to accommodate a range of deposition rates. For example, a plasma head of the type shown in Figures 1 and 2, with a power input
5 between 1 and 10 kW, may provide a material deposition rate of up to around 1 kg/hour.

In order to avoid exposure of hot or molten metal or alloy to the atmosphere and overall maintain clean processing conditions, the plasma head and work-piece may be
10 enclosed within a chamber that is vacuum-pumped and/or flushed with an Inert gas. The vacuum chamber may be equipped with means for removing iodine vapor produced by the decomposition of the one or more metal iodides, or excess metal iodides, for example, by condensation on a suitably disposed cold surface.

In Figures 1 and 2, plasma head **10** is shown disposed a vertical distance Z_H above a
15 horizontal substrate or work-piece surface **8**. In general, the plasma head need not be disposed vertically above the work-piece. The work-piece surface region **8** is also shown as significantly larger than the lateral dimension X_D of deposited material **7**, though this need not be the case.

In Figure 2, the furthest extent of the external plasma arc is shown at a distance Z_P
20 from plasma head **10**, with the remainder of the distance to the work-piece, shown as Z_G , constituting a gas or gas mixture flow, as shown as dashed arrows **G**. The plasma head may be operated such that only a small fraction of the flow of the gas or gas mixture exiting the plasma head actually reaches the work-piece, for example, by

operating the plasma head vertically above the work-piece and maximizing distance Z_G , such that a portion of the metal or alloy may reach the work-piece through the action of gravity.

The combined flow rate, work-piece to plasma head distance Z_H , internal and external
5 plasma conditions, including the distances Z_P and Z_G , and composition of the flow mixture may be adjusted to deposit a metal or alloy powder onto the work-piece. For example, Ti or alloy Ti alloy powder may be collected on a work-piece maintained at a sufficiently low temperature, typically no more than about 300 °C, to avoid the powder from coalescing, facilitating retrieval for possible use in additive manufacturing and
10 other powder metallurgical technologies. The work-piece may be actively cooled to facilitate formation of a sufficiently friable powder agglomeration.

The plasma head may be displaced and/or rotated relative to the work-piece in a controlled manner, and the work-piece may also be translated and/or rotated relative to the plasma head in a controlled manner, to facilitate access to different work-piece
15 locations and allow deposition on selected regions. For a fixed deposition rate and plasma head to work-piece distance, the thickness of the deposited material, as shown by Z_D in Figures 1 and 2, will be determined by the deposition time, and the lateral extent of the deposited material, as shown by X_D in Figures 1 and 2, by the lateral extent of the material flow at the work-piece surface. For a fixed deposition rate and
20 plasma source to work-piece distance, shown as Z_H in Figures 1 and 2, uniform linear motion of a stable plasma source during deposition, for example, from X_0 to X_1 in Figure 1 may form a line of deposited material on work-piece surface **8**, shown by the dashed lines representing intermediate stages. A series of abutting lines or points may

be deposited on original work-piece surface **8**, by controlled relative motion of work-piece and plasma head, to form a continuous or semi-continuous first layer of material having a complex lateral shape, as shown by feature **17** in Figure 2. Once allowed to solidify and cool, as necessary, such a first layer may provide a new surface for
5 deposition of more material, as shown in Figure 2 by the location of deposited material **7** on first layer **17**.

Using known additive-manufacturing control techniques for successive layers, including by taking account of the effects on deposition and cooling rate of changes in sample shape, a three-dimensional shaped component may be formed. Thus, the
10 work-piece and plasma head may be used for additive manufacturing of metal or alloy components.

Claims

1. A method for forming a material comprising a first metal, comprising the following steps:

furnishing a work-piece and a plasma head comprising a plasma
5 generation volume;

establishing a first flow comprising an inert gas traversing the plasma
generation volume and plasma head;

applying a plasma voltage across the plasma generation volume to
establish a plasma arc comprising an internal portion confined within the
10 plasma head;

establishing a second flow comprising a first metal iodide configured to
combine with the first flow and traverse at least a portion of the plasma arc;
characterized by:

regulating the first and second flows and plasma power to fully
15 decompose at least a substantial fraction of the first metal iodide in the
combined flow;

directing at least a fraction of the combined flow comprising the at least
a substantial fraction of fully decomposed first metal iodide to contact a region
of a surface of the work-piece; and

20 depositing a material comprising the first metal on at least a fraction of
the region.

2. The method of claim 1, further comprising forming an external portion of the
plasma arc extending outside the plasma head.

3. The method of claim 2, further comprising contacting at least a fraction of the
25 region with the external portion of the plasma arc.

4. The method of claim 3, further comprising establishing a transfer voltage between the work-piece and plasma head to form a transferred plasma arc.

5. The method of any of claims 1 to 4, wherein the second flow comprising the first metal iodide combines with the first flow before exiting the plasma generation volume.

6. The method of any one of claims 1 to 4, wherein the second flow comprising the first metal iodide combines with the first flow before exiting the plasma head.

7. The method of any of claims 1 to 4, wherein the second flow comprising the first metal iodide combines with first flow in the external portion of the plasma arc.

8. The method of any one claims 5 to 7, further comprising:

establishing a third flow comprising a second metal iodide configured to combine with the first flow and traverse at least a portion of the plasma arc; characterized by:

regulating the first, second and third flows and plasma power to fully decompose at least a substantial fraction of the first and second metal iodides in the combined flow;

directing at least a fraction of the combined flow comprising the at least a substantial fraction of fully decomposed first and second metal iodides to contact a region of a surface of the work-piece; and

depositing a material comprising an alloy of the first and second metals on at least a fraction of the region.

9. The method of claim 8, wherein the third flow comprising the second metal iodide combines with the first flow before exiting the plasma generation volume.

10. The method of claim 8, wherein the third flow comprising the second metal iodide combines with the first flow before exiting the plasma head.

11. The method of claim 8, wherein the third flow comprising the second metal iodide combines with first flow in the external portion of the plasma arc.

5 12. The method of claims 8 to 11, further comprising:

establishing a fourth flow comprising a third metal iodide configured to combine with the first flow and traverse at least a portion of the plasma arc;

regulating the first, second, third and fourth flows and plasma power to fully decompose at least a substantial fraction of the first, second and third metal iodides in the combined flow;

directing at least a fraction of the combined flow comprising the at least a substantial fraction of fully decomposed first, second and third metal iodides to contact a region of a surface of the work-piece; and

depositing a material comprising an alloy of the first, second and third metals on at least a fraction of the region.

13. The method of claim 12, wherein the fourth flow comprising the third metal iodide combines with the first flow before exiting the plasma generation volume.

14. The method of claim 12, wherein the fourth flow comprising the third metal iodide combines with the first flow before exiting the plasma head.

15. The method of claim 12, wherein the fourth flow comprising the third metal iodide combines with first flow in the external portion of the plasma arc.

16. The method of any of claims 1 to 15, wherein at least one of the metal iodide flows comprises at least a substantial fraction of metal iodide in a solid phase when it combines with the first flow.

17. The method of any of claims 1 to 15, wherein at least one of the metal iodide flows comprises at least a substantial fraction of metal iodide in a liquid phase when it is combined with the first flow.
18. The method of any of claims 1 to 15, wherein at least one of the metal iodide flows comprises at least a substantial fraction of metal iodide in a vapor phase when it is combined with the first flow.
19. The method of any one of claims 1 to 18, wherein the first metal iodide is selected from the group consisting of TiI_4 , ZrI_4 and BeI_2 .
20. The method of any one of claims 8 to 19, wherein the second metal iodide is selected from the group consisting of VI_3 , AlI_3 , ZrI_4 , BeI_2 , HfI_4 , NbI_3 , TaI_3 , BiI_3 , SiI_4 , SnI_2 , GdI_3 , NdI_3 , ThI_4 , MoI_2 , CoI_2 , NiI_2 , MgI_2 , SnI_4 and Cl_4 .
21. The method of any one of claims 12 to 20, wherein the third metal iodide is selected from the group consisting of VI_3 , AlI_3 , ZrI_4 , BeI_2 , HfI_4 , NbI_3 , TaI_3 , BiI_3 , SiI_4 , SnI_2 , GdI_3 , NdI_3 , ThI_4 , MoI_2 , CoI_2 , NiI_2 , MgI_2 , SnI_4 and Cl_4 .
22. The method of any one of claims 1 to 21, further comprising delivering into the combined flow exiting the plasma head microwave energy having a frequency spectrum and power selected to break apart at least one metal-iodine species.
23. The method of any one of claims 1 to 22, further comprising combining a flow of a seeding material into the combined flow to condense clusters comprising the one or more metals in the at least a fraction of the combined flow comprising at least a substantial fraction of the one or more fully decomposed metal iodides.
24. The method of claim 23, wherein the seeding material traverses at least a portion of the internal portion of the plasma arc.
25. The method of claim 23, wherein the seeding material traverses at least a portion of the external portion of the plasma arc.
26. The method of claim 23, wherein the seeding material does not traverse a portion of the plasma arc.

27. The method of any one of claims 23 or 26, wherein the seeding material comprises metal particles.

28. The method of claim 27, wherein the metal particles comprise a metal selected from the group consisting of Al, V, Si, B, Mo, Be and Ti.

5 29. The method of any one of claims 23 to 26, wherein the seeding material comprises ceramic particles.

30. The method of claim 29, wherein the ceramic particles comprise a ceramic selected from the group consisting of TiB_2 , SiC, WC, BN, Y_2O_3 and ZrO_2 .

10 31. The method of any one claims 1 to 30, wherein the at least a portion of the fraction of the combined flow contacting the region further comprises hydrogen.

32. The method of claim 31, wherein one or more of the first, second, third or fourth flows further comprises hydrogen.

15 33. The method of any one of claims 1 to 32, wherein the material deposited on the region is deposited in a molten state.

34. The method of any one of claims 1 to 32, wherein the material deposited on the region is deposited in a solid state.

35. The method of any of claims 1 to 34, further comprising applying heat from an additional source to the deposited material.

20 36. The method of any one of claims 1 to 35, further comprising applying a controlled relative motion of plasma head and work-piece during deposition to form successive layers of deposited material in different regions of the work-piece and create a shaped component.

25 37. The method of any one of claims 1 to 36, further comprising surrounding the flow from the outlet to the work-piece with an inert gas shield.

38. A system for implementing the method of claims 1 to 37, wherein the plasma generation volume is defined by an outer surface of an elongated cathode and

an inner surface of a coaxially disposed anode, and wherein the first flow comprising an inert gas passes through a first opening formed in a lower surface of the plasma head.

39. The system of claim 38, wherein the plasma head further comprises a substantially coaxial shield and a substantially annular opening disposed coaxially with respect to the first opening in the lower surface of the plasma head, and wherein a coaxial volume is defined by an outer surface of the anode and an inner surface of the shield and configured to deliver a gas flow from an upper portion of the plasma head through the annular opening.

40. The system of claim 39, wherein the flow from the annular opening is configured to intersect the first flow exiting the first opening.

41. The system of claim 39, wherein the flow from the annular opening is configured to be substantially parallel with and enclose the first flow from the first opening.

42. The system of any of claims 38 to 41, wherein the plasma head comprises a feeder for directing at least one metal iodide flow into the coaxial volume.

43. The system of any of claims 38 to 42, wherein the plasma head comprises a feeder for directing at least one metal iodide flow into the plasma generation volume.

44. The system of any of claims 38 to 43, further comprising a feeder disposed for directing at least one metal iodide flow into the external portion of the plasma arc.

45. The system of any of claims 38 to 44, further comprising an induction source disposed to deliver microwave energy to the combined flow from the plasma head.

46. The system of any of claims 38 to 45, further comprising a means for delivering at least one additional material flow directly into the deposited material on the region.

47. The system of any of claims 38 to 46, further comprising a heat source configured to deliver heat directly to the deposited material on the region.

48. The system of any of claims 38 to 47, further comprising control mechanisms for translating the work-piece and the plasma head.

5 49. The system of any of claims 38 to 48, further comprising a vacuum-pumped chamber housing the work-piece and plasma head.

50. The system of any of claims 38 to 49, further comprising a means for condensing iodine disposed in the vacuum chamber.

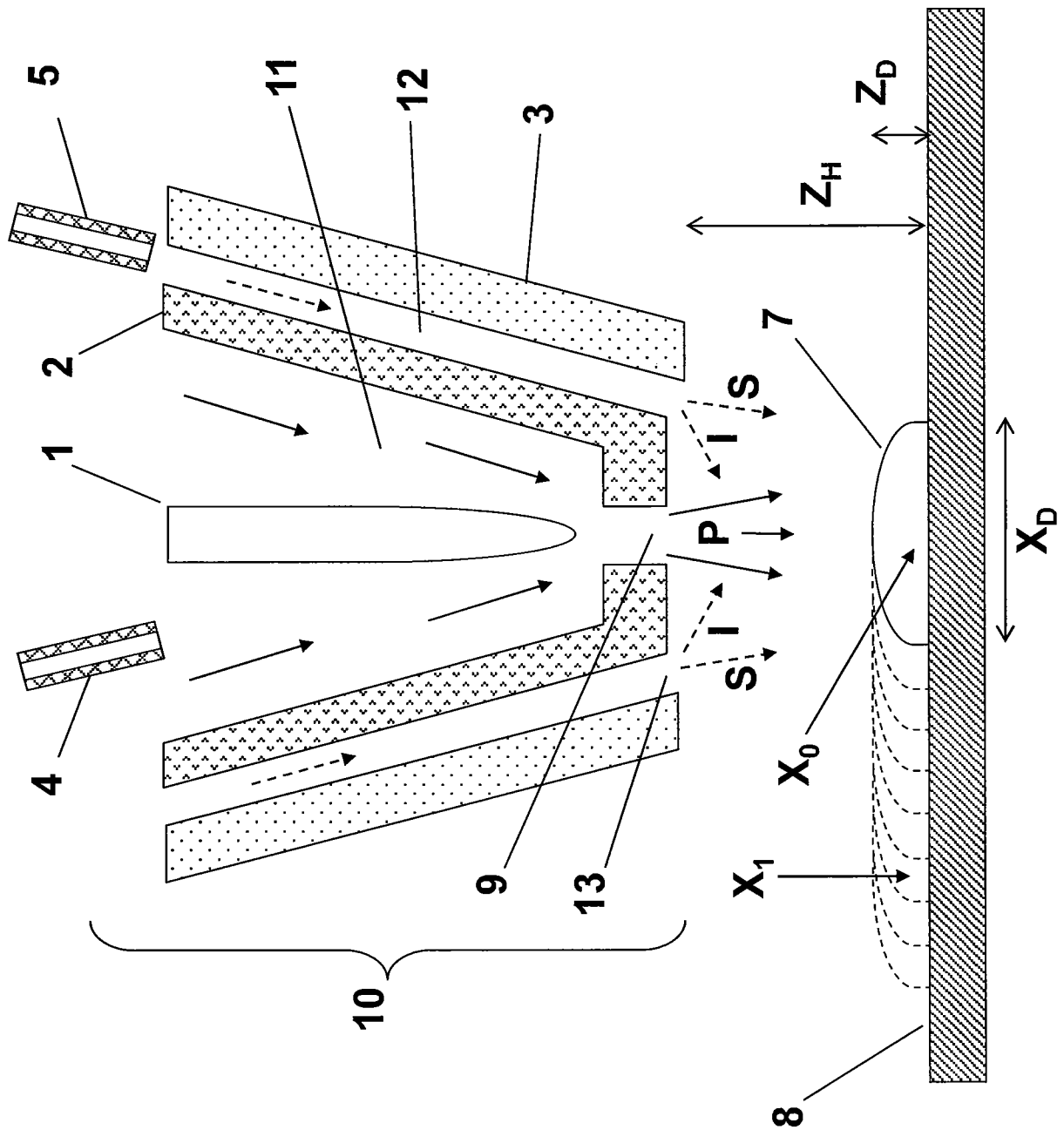


FIG. 1

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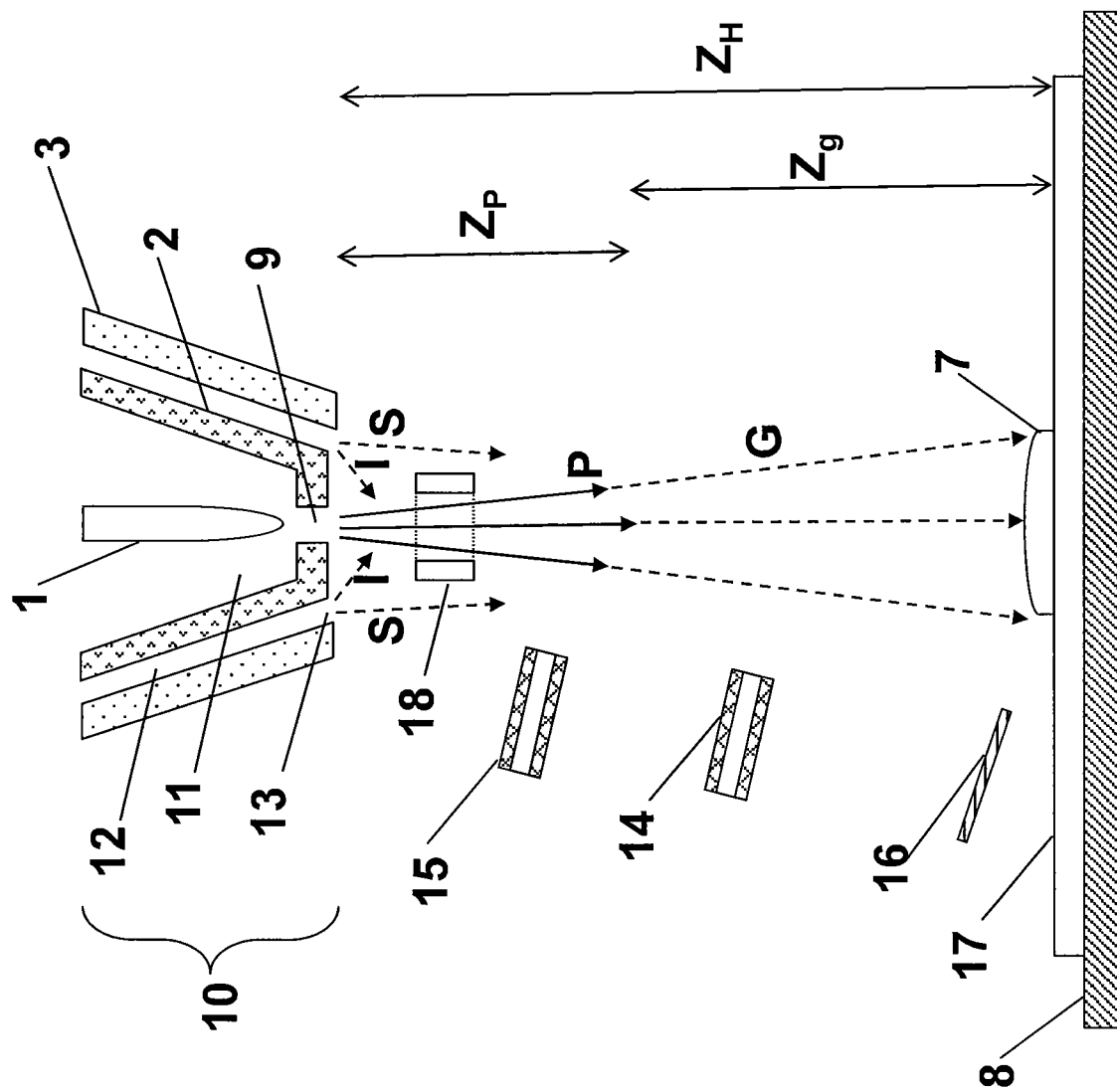


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/056798

A. CLASSIFICATION OF SUBJECT MATTER INV. C23C16/06 C23C16/513 B05B7/22 C23C4/12 C22B34/12 H05H1/42 H01J37/32 ADD. According to International Patent Classification (IPC) or to both national classification and IPC																	
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C23C B05B C22B H05H H01J Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, INSPEC, WPI Data																	
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;"> Funsho H Ojebuoboh: "EXPERIMENTAL PLASMA SYSTEM FOR TiI4 DISPROPORTIONATION (Chapter 4); RESULTS AND DISCUSSIONS (Chapter 5)" In: "An assessment of titanium metal production in a plasma reactor by TiI4 disproportionation (Dissertation)", 1 January 1985 (1985-01-01), Colorado School of Mines., 1985, XP55040279, cited in the application </td> <td style="text-align: center; vertical-align: top;">38,43,44</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;">the whole document</td> <td style="text-align: center; vertical-align: top;">1-37, 45-48</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;"> ----- EP 0 703 302 A1 (PLAS PLASMA LTD [IL]) 27 March 1996 (1996-03-27) </td> <td style="text-align: center; vertical-align: top;">38-44</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">Y</td> <td style="vertical-align: top;"> page 3 - page 4; figures 1-4 ----- -/-- </td> <td style="text-align: center; vertical-align: top;">1-37</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	Funsho H Ojebuoboh: "EXPERIMENTAL PLASMA SYSTEM FOR TiI4 DISPROPORTIONATION (Chapter 4); RESULTS AND DISCUSSIONS (Chapter 5)" In: "An assessment of titanium metal production in a plasma reactor by TiI4 disproportionation (Dissertation)", 1 January 1985 (1985-01-01), Colorado School of Mines., 1985, XP55040279, cited in the application	38,43,44	Y	the whole document	1-37, 45-48	X	----- EP 0 703 302 A1 (PLAS PLASMA LTD [IL]) 27 March 1996 (1996-03-27)	38-44	Y	page 3 - page 4; figures 1-4 ----- -/--	1-37
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.															
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.																	
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Date of the actual completion of the international search 10 December 2012		Date of mailing of the international search report 17/12/2012															
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Schuhmacher, Jörg															

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International application No
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