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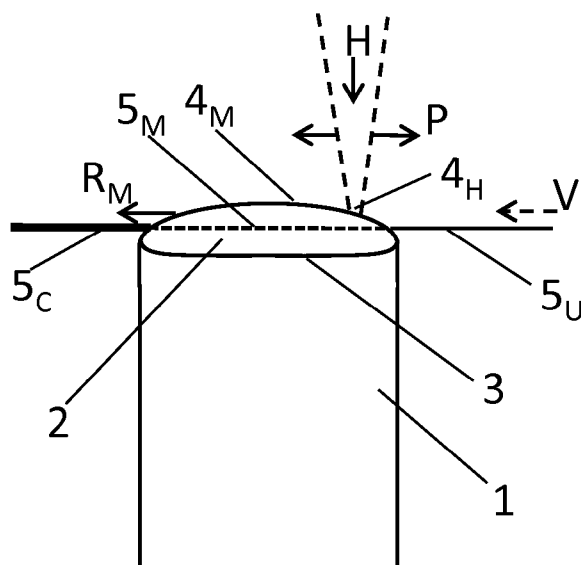


FIG. 1

(57) Abstract: A method and system are disclosed for producing a wire including a core and one or more different multi-elemental coatings suitable for use in additive manufacturing and other applications. An elongated heat-resistant core is coated by passing it longitudinally through one or more melt pools formed by applying one or more directed heat sources to the upward-facing surfaces of one or more consolidated elemental blocks having one or more defined average elemental compositions. The coated core, once cooled to form wire, may be stored or used directly in additive manufacturing or other applications.

METHOD AND SYSTEM FOR PRODUCING AND USING WIRES INCLUDING A CORE AND MULTI-ELEMENTAL COATING

FIELD OF THE INVENTION

- 5 The present invention relates to the production of wires including a core and a multi-elemental coating. The present invention also relates to the use in additive manufacturing and other applications of such wires.

BACKGROUND OF THE INVENTION

- 10 Wires that include a core and a multi-elemental coating are useful in a wide range of applications, including as feedstock in additive manufacturing and as constituents in structural and other composite materials.

In additive manufacturing, the wire, either coated or uncoated, is melted by a
15 directed heat source, typically a laser, plasma arc or electron beam, to deposit successive layers of material. Uncoated multi-elemental wires are expensive to produce by conventional methods, such as extrusion processing, which requires large amounts of energy and is applicable only to ductile alloys.

- 20 Wires that include a core and a multi-elemental coating are also expensive to produce using known methods, such as coating an elongated core by passing it longitudinally through a region of molten alloy formed by induction heating.

In US Pat No. 5,662,969, an AlZn alloy charge in a crucible is melted by induction
25 heating to form a convex meniscus at its surface, through which an elongated steel core is passed longitudinally. The process is expensive because energy is needed to maintain the entire alloy charge in a molten state during the coating process, while only a fraction of the charge is applied as coating.

- 30 In US Pat. No. 6,174,570, the end of Ti alloy bar projecting through the base of a crucible is melted and a meniscus formed, again using induction heating, and a SiC filament passed longitudinally through the Ti alloy meniscus. See Fig. 7 and 8:56 to 10:51. Though less than the entire Ti alloy bar is melted at one time, the process is expensive, since a significant amount of energy is needed to produce
35 the Ti alloy bar. It is also limited to materials which are available as alloy bars.

Separately, it is known to produce multi-elemental blocks having a defined average composition from consolidated but substantially unalloyed constituents. For example, consolidated elemental blocks ("CEBs") with defined average
5 compositions corresponding to certain Ti-Al and Ti-Al-Nb alloys used in casting and as consumable electrodes in vacuum arc remelting have been formed by placing, in a cylindrical mould, appropriate proportions of 4-15 mm pieces of Ti sponge, 250-400 μm Al powder, 40-60 μm Nb powder and 2-10 mm pieces of Nb-Al master alloy, applying weight, preheating to 700 °C and reactively sintering at
10 between 1100-1300°C. See Andreev et al., Int'l. J. of SHS, Vol. 17, No. 2, pp 136-143 (June 2008). CEBs have with a range of other compositions have been formed using similar or related techniques, though are not always referred to by that name.

15 An improved low-cost method and system for forming wires including a core and a multi-elemental coating having a defined composition, suitable for use in additive manufacturing and other applications, would be advantageous.

OBJECT OF THE INVENTION

20 It is an object of at least some embodiments of the present invention to provide a method and system for rapidly and economically forming lengths of wire including a core surrounded by one or more coating layers including material from one more consolidated elemental blocks ("CEBs") having one or more defined average elemental compositions.

25

It is another object of at least some embodiments of the present invention to provide wires including a core surrounded by one or more coatings having one or more defined average elemental compositions suitable for use in range of applications, including additive manufacturing.

30

It is a further object of at least some embodiments of the present invention to provide an integrated method and system for producing wires including a core surrounded by one or more coatings having one or more defined compositions and for using such wires in additive manufacturing.

35

It is a further object of the present invention to provide an alternative to the prior art.

SUMMARY OF THE INVENTION

5 Thus, the above described objects and several other objects are intended to be obtained in a first aspect of the invention by providing a method for producing a wire including a core and a multi-elemental coating, the method including: furnishing a CEB having a defined average elemental composition; applying a directed heat source to an upward facing surface of the CEB to form a melt pool
10 having substantially the defined average elemental composition; passing a length of elongated heat-resistant core in a substantially longitudinal direction through the melt pool to apply to the length of heat-resistant core a coating including material from the melt pool; and, cooling the length of coated core to form a length of wire including a core surrounded by a coating having substantially the
15 defined average elemental composition.

A CEB having a defined average elemental composition (a "defined composition") means a block of constituents, sufficiently consolidated to allow formation of a melt pool on an upward-facing block surface but substantially unalloyed, and
20 having, averaged over the entire block, a defined elemental composition. The constituents of a CEB may be elemental metals, semi-metals or non-metals, or compounds, mixtures or alloys of such materials, and may be in one or more different forms, e.g., powders, granules, particles, shavings, pieces or sponge. Substantially unalloyed means that a substantial fraction of the constituents are
25 not alloyed by the consolidation process. The defined average elemental composition of a given CEB may be determined from knowledge of the composition of the constituents and their relative proportions.

A CEB having a defined composition may have been formed from appropriate
30 proportions a given set of constituents using a number of related processes, such as reactive sintering, reactive sintering under axial pressure with an optional thermal pretreatment, isostatic pressing without additional heat input, hot isostatic pressing ("HIPping"), and self-propagating high-temperature synthesis ("SHS").

An advantage of producing wires including a core and a coating having substantially the defined composition of a CEB is that wires including a core and a multi-elemental coating with a range of compositions can be produced rapidly at low cost.

5

A directed heat source means a source capable, at a minimum, of delivering a given total heat flow into a given surface area. A directed heat source may be further capable of delivering a range of total heat flows and heat flow profiles, i.e., spatial and/or temporal variations in heat flow, across all or part of an upward-
10 facing CEB surface.

The upward-facing CEB surface to which the directed heat source is applied need not have been a surface nor upward-facing during formation of the CEB, need not be uniformly flat or horizontal, and may include molten and/or solid portions.

15

An advantage of applying a directed heat source to an upward-facing CEB surface is the ability to selectively melt at one time only that fraction of the CEB necessary to form a melt pool having a given temperature, size and shape suitable for application of a coating to the elongated core.

20

Melt pool size means the total amount of molten material constituting the melt pool. Melt pool shape means the overall shape of the melt pool, as defined by the melt pool surface, which forms at least part of the upward-facing CEB surface, and the interface between the melt pool and the solid portion of the CEB. Melt pool
25 temperature means a temperature representative of the temperature distribution within the melt pool, generally between the maximum, adjacent to the melt pool surface where heat flow is delivered, and minimum, adjacent to the solid portion of the CEB remote from the melt pool surface.

30 Passing the elongated core in a substantially longitudinal direction includes movement by drawing, i.e., pulling, or pushing, or both, and may include intermittent and/or continuous movement at a substantially fixed or variable rate. Passing the elongated core through the melt pool in a substantially longitudinal direction means movement with a substantial longitudinal component of at least
35 that portion of elongated core within the melt pool between its entry into and exit

from the melt pool. The portion of elongated core within the melt pool at any one time need not be perfectly straight, nor, over a period of time, describe a single substantially fixed path between entry and exit from the melt pool.

- 5 Depending on the shape of the melt pool surface, e.g., in the event it has a depressed central region, a portion of the core length passing through a melt pool may exit and enter the same melt pool more than once. The motion of core portions not within the melt pool may be substantially longitudinal with respect to the elongated core but aligned along a range of different directions, as a result of
- 10 curvature or bending of the path of the elongated core, and may, in some portions, also include a substantially non-longitudinal component.

A heat-resistant elongated core is one that retains sufficient structural integrity, during and after passage through the melt pool, coating and cooling, to form part

15 of a wire suitable for use in additive manufacturing or other applications. The required degree of heat resistance may vary, depending on the combination of materials used in the core and the one or more coating layers.

Cooling of the length of coated core is meant to include passive cooling, e.g.,

20 radiative cooling once remote from the directed heat source, and/or active cooling, e.g., directing at the coated core a stream of suitably chemically neutral gas, such as argon or possibly nitrogen, depending on the core and coating composition.

- 25 The heat resistant core may be a filament or flexible strip.

An advantage of using a filament or flexible strip is that a range of heat-resistant materials are available as filaments or strips.

- 30 The directed heat source may deliver heat using an electron beam, a laser beam, a focused incoherent light source, or a plasma.

An advantage of delivering heat using electron or light beams is that a great range of total heat flows and heat flow profiles may be delivered by focusing,

moving and scanning the beam. A further advantage of light beams is that these do not require operation under reduced pressure or vacuum.

The method may further comprise applying the coating at a substantially uniform
5 rate by regulating one or both of the melt pool temperature and the speed of passage of the elongated core through the melt pool.

Regulating is used to mean varying in a controlled manner or maintaining substantially constant.

10

Regulating one or both of the melt pool temperature and the speed of passage of the elongated core through the melt pool may include monitoring the rate at which the coating is applied and monitoring and adjusting accordingly one or both of the melt pool temperature and the speed of passage of the elongated core. The
15 temperature of the melt pool may be monitored by measuring the temperature at one or more regions of the melt pool. The temperature of the melt pool may be regulated by regulating the application of the directed heat source.

An advantage of applying the coating at a substantially uniform rate is that wires
20 may be formed having a coating that is longitudinally uniform and thus suitable for applications such as additive manufacturing, in which radial variations in coating thickness may not be critical.

The method may further comprise maintaining substantially constant one or more
25 of the temperature, size and shape of the melt pool by regulating the application of the directed heat source.

An advantage of maintaining substantially constant one or more of the melt pool temperature, size or shape is that process stability may be enhanced and a
30 greater continuous length of core coated.

Regulating application of the heat source means regulating one or both of the total heat flow and the heat flow profile, which may include regulating the relative position of the upward-facing CEB surface and the directed heat source,

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The method may further comprise maintaining substantially constant the length of the path of the elongated core within the melt pool.

5 An advantage of maintaining substantially constant the length of the path of the elongated core within the melt pool is that process stability may be enhanced and a greater continuous length of core coated.

The method may further comprise applying the coating with a substantially uniform radial thickness by configuring the elongated core to exit the melt pool
10 substantially close to a surface normal direction.

An advantage of applying the coating with a substantially uniform radial thickness is that wires suitable for a greater range of applications, those in which substantial radial thickness variations may not be tolerated, may be produced.

15

The size and shape of the melt pool and the shape of a solid portion of the upward-facing CEB surface may be configured to form a lip of solid material surrounding the melt pool.

20 An advantage of a lip of solid material is that loss of melt pool material by spillage may be minimized, process stability enhanced, and a greater fraction of a CEB coated onto a length of core.

The method may further comprise configuring a portion of the lip to facilitate
25 entry of the elongated core into the melt pool and/or a portion of the lip to facilitate exit of the coated elongated core from the melt pool.

Advantages of configuring portions of the lip to facilitate entry or exit of the core into or from the melt pool include improvement of process stability while
30 minimizing loss of molten material through spillage.

An advantage of configuring a portion of the lip solely to facilitate entry of the core into the melt pool is improved control over shape of the melt pool in the region where the coated core exits.

35

The method may further include: furnishing one or more additional CEBs; applying one or more directed heat sources to each of one or more upward-facing surfaces of each of the one or more additional CEBs to form one or more melt pools; passing the at least a fraction of the length of coated core in a substantially longitudinal direction successively through the one or more melt pools to apply one or more coatings including material from the one or more melt pools; and cooling the length of twice or more coated core to form a length of wire including a core surrounded by a coating having substantially the defined composition and one or more additional coatings.

10

The additional CEBs may have the defined composition or may have one or more additional defined compositions.

Advantages of successively coating the core with material from one or more additional CEBs optionally having one or more additional defined compositions include the ability to increase coating thickness and form wires with radially graded compositions.

The method may further include using the lengths of wire in a range of applications, including in additive manufacturing, in which at the least a fraction of the length of wire is fed towards a work-piece surface, a work-piece-directed heat source is applied to melt the at least a fraction of the length of wire and the molten material from the at least a fraction of the length of wire is incorporated into the work-piece surface.

25

Advantages of using lengths of wire formed using the above methods in additive manufacturing, in which the wire including core and coating is melted, is that radial non-uniformity and substantial intermixing between core and coating during production of the wire may be accommodated.

30

In another embodiment, a system is provided for producing a wire according to the above methods, including: a directed heat source configured to form a melt pool on an upward-facing surface of a consolidated elemental block having a defined composition; a core feeder configured to pass a length of elongated core in a substantially longitudinal direction through the melt pool and a wire receiver

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configured to receive the length of core and multi-elemental coating having substantially the defined composition.

An advantage of such a system is that wires including a core and a multi-
5 elemental coating having substantially the defined composition may be produced rapidly and inexpensively.

The system may further include a work-piece-directed heat source, a wire feeder and a work-piece mounting stage, configured for additive manufacturing.

10

An advantage of such an integrated system is that additive manufacturing can be performed economically using a continuous supply of wire of a required composition, corresponding to the core composition and the substantially defined composition of the coating.

15

In other embodiments, wires including a core surrounded by one or more multi-elemental coatings are provided, suitable for a range of applications including additive manufacturing, near net-shape manufacturing, production of shaped wire forms for HIPping—see, e.g., application EP13164676.2, entitled Wire Hipping,
20 filed 22 April 2013, which is hereby incorporated by reference—the production of thermoelectrics, magnets, superconductors or other functional materials.

The various aspects of the present invention may each be combined. These and other aspects of the invention will be apparent from and elucidated with reference
25 to the embodiments described hereinafter.

BRIEF DESCRIPTION OF THE FIGURES

The figures show one way of implementing the present invention and are not to be construed as being limiting on other possible embodiments falling within the
30 scope of the attached claim set.

Figure 1 shows schematically part of a system for performing a coating method according to the present invention.

Figures 2A and 2B show schematically a CEB and melt pool formed according to the present invention.

Figures 3A and 3B show schematically side and top views of part of a system for performing a coating method according to the present invention.

Figure 4 shows schematically a side view of part of a system for performing a coating method using two consolidated elemental blocks according to the present invention.

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Figure 5A and 5B show schematically cross sections through wires made according to the present invention.

DETAILED DESCRIPTION OF AN EMBODIMENT

15 Fig. 1 is a schematic side view of part of a system for applying a coating to an elongated core according to the present invention. A section through a CEB is shown to include a solid portion **1** having a defined composition and, at the upper surface of the CEB, a melt pool **2** having substantially the defined composition and formed by the action of a directed heat source, shown as delivering a total heat flow **H** into a heat delivery area **4_H** located on melt pool surface **4_M**. The CEB in Fig. 1 has the form of a solid cylinder, with a circular, substantially flat and horizontal upward-facing surface. Such a cylindrical CEB may have a range of aspect ratios and sizes, e.g., 1 to 10 cm in diameter and 10 to 20 cm in height.

25 In general, CEBs may be furnished in a range of shapes and sizes, with a range of defined compositions, including any required number of elements, and may have been formed using a variety of different processes—e.g., reactive sintering, reactive sintering under axial pressure with an optional thermal pretreatment, isostatic pressing without additional heat input, HIPping, SHS processing, with each process optionally performed under a controlled atmosphere—from constituents of a range of different material types—e.g., elemental metals, semi-metals or non-metals, or compounds, mixtures or alloys of such materials—in one or more different forms—e.g., powders, granules, particles, shavings, pieces or sponge.

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Any local variations in the distribution of constituents within the CEB—arising, e.g., from the presence of large constituent pieces or from preferential segregation of constituents—may cause local regions of the CEB to depart more than substantially from the defined composition. The effect of such compositional variations on melt pool composition may be mitigated by melting a sufficiently large region of the CEB to produce a melt pool having substantially the defined composition. A CEB may also be melted in a neutral atmosphere or under vacuum, in order to minimize the introduction of contaminants or suppress oxidation, and may be at least partly contained in a crucible to contain any spillage of molten material.

In Fig. 1, the total heat flow into area 4_H is shown schematically by arrow H and the heat flow profile by arrows P extending from heat delivery area 4_H . Arrows P may indicate a time-dependent variation of one or more of the size, shape or position of heat delivery area 4_H , or a change in the temporal and spatial distribution of total heat flow H within heat delivery area 4_H . By applying a range of total heat flows and heat flow profiles, melt pools may be formed having a range of temperatures, sizes and shapes. Total heat flows and heat flow profiles may be chosen to promote intermixing and to enhance the compositional and thermal uniformity of the melt pool.

In general, the application to an upward-facing CEB surface of a directed heat source that employs an electron or optical beam may be regulated. The total heat flow may be regulated by adjusting the power of the beam, and the heat flow profile may be regulated by steering or focusing the beam to vary the size, shape and position at the beam at the upward-facing CEB surface. For electron and optical sources, the heat flow profile may be further regulated by rapidly scanning the beam across the upward-facing CEB surface to deliver the total heat flow into any of range of different shaped areas or, if the beam may be effectively blanked, into more than one area. Where allowed by the configuration of heat source and CEB, the total heat flow and heat flow profile at the upward-facing CEB surface may be varied by changing the relative displacement between directed heat source and CEB surface. With plasma sources, to the extent that steering and focusing the beam may be more difficult to accomplish, greater reliance on relative displacement of the heat source and CEB surface may be required.

With conventional heat sources, a mean melt pool temperature in excess of 3500°C may be readily attained, which is above the melting point of virtually all possible constituents and defined compositions. On the other hand, not all CEB
5 constituents need be melted, since granules or particles may enter the melt pool and be coated onto the elongated core together with the molten material. A schematic cross section through a wire including core **5** surrounded by a coating **C** of uniform radial thickness **T** containing granules **G** is shown in Fig. 5B.

10 The size of a melt pool formed at a given upward-facing CEB surface, may be controlled by regulating the application of the directed heat source. For example, using any of a number of directed heat sources, an approximately 0.5-1 cm deep melt pool may be formed to extend across all or part of a circular CEB surface up to about 10 cm in diameter.

15

The shape of a melt pool formed at a given upward-facing CEB surface may also be controlled by regulating the application of the directed heat source. However, the physical properties of the material in the melt pool, e.g., surface tension, viscosity, thermal conductivity, and the solid portion, e.g., thermal conductivity,
20 and phenomena occurring in and around the melt pool, e.g., convection flows, mass transport across the solid-melt pool interface, may limit the range of achievable melt pool shapes. Further, to the extent that the relevant physical properties and phenomena are interrelated and dependent on factors such as the temperature distribution within and around the melt pool, it may not be possible
25 to vary melt pool temperature, size and shape completely independently of one another. Nevertheless, by suitable regulation of the application of the directed heat source to a given CEB upward-facing surface, a range of melt pool temperatures, sizes and shapes, suitable for passage of the elongated core in a substantially longitudinal direction and application of a coating, may be realised.
30 Regulation may include monitoring of the melt pool temperature, size and shape and suitable adjustment to one or both of the total heat flow and heat flow profile.

In Fig. 1, melt pool **2** is shown bounded by a convex interface **3** and a convex surface **4_M** extending to the edge of the upward-facing CEB surface, while in Fig.
35 2A melt pool **2** is bounded by a convex interface **3** and a convex surface **4_M** not

extending across the entire upward-facing CEB surface, and thus leaving an exposed solid surface region **4_B**. A length of elongated heat-resistant core **5** is shown passing through the melt pool **2** in a substantially longitudinal direction at speed **V**. Uncoated core portion **5_U** is shown before entry into melt pool surface **4_M**, portion **5_M** within melt pool **2**, and coated portion **5_C** after exiting melt pool surface **4_M**. The rate at which material leaves melt pool **2** to form coated core **5_C** is indicated by arrow **R**. Solidification upon cooling of the molten coating to form a wire is not shown. In any event, once sufficiently cooled, either passively and/or actively, the wire may be spooled for storage and later use or fed directly for use in the required application, e.g., in additive manufacturing. The heat flow profile of the directed heat source applied to the upward-facing CEB surface may be configured to take account of the elongated core, e.g., to deliver heat to uncoated core portion **5_U**, in order to minimize the formation of temperature gradients upon its entry into melt pool **2**, or to minimize heat delivery to coated core portion **5_C**, in order not to inhibit cooling and solidification of the molten coating.

A given heat-resistant elongated core may have a range of sizes and cross sectional shapes, so long as it offers sufficient flexibility, mechanical strength and heat-resistance to sustain passage through a melt pool having substantially the defined composition. For example, the core may be a filament with a diameter up to around 100 μm , with a substantially circular or oval cross section, formed from a range of heat-resistant materials, such as elemental metals, e.g., Mo or W, non-metals, e.g., B, alloys, or ceramics, e.g., SiC, or may be a strip formed from such materials. The particular core material chosen may depend on its compatibility with the defined composition of the CEB. Some penetration of the coating into core, or reaction between core and coating may be accommodated, depending to some extent on the application to which the wire is put, so long as the wire retains sufficient structural integrity for its intended use.

The choice of heat source, e.g., electron beam, laser, plasma source, or incoherent light source, may depend on the total heat flow and heat flow profile required for a particular application, and on whether the source is to be operated in vacuum or under a controlled atmosphere.

The rate **R** at which material from melt pool **2** is applied to the exiting length of core may vary as a function of the speed **V** at which the core passes through the melt pool and the viscosity, and other properties, of the material in the melt pool **2**. To the extent that the viscosity, and other relevant properties, of the material in melt pool **2** are dependent on temperature, the rate **R** at which material from melt pool **2** is applied to the exiting core may be regulated, i.e., varied in a controlled manner or maintained substantially constant, by regulating one or more of the speed of passage **V** of the elongated core and the temperature of the melt pool. The rate at which material is applied may be monitored by measuring the amount of coating applied along the length of the wire and may be regulated by adjusting the speed of passage **V** of the elongated core and the temperature of the melt pool. Melt pool temperature may be regulated by regulating the application of the directed heat source, as discussed above. The applied coating layer may be of the order of up to around 100 μm in thickness, though the coating layer thickness need not be radially uniform.

In order to, for example, increase process stability, it may be advantageous to maintain substantially constant one or more of the melt pool temperature, size or shape during the coating process.

20

For example, referring to Fig. 1, once the directed heat source has been applied to the upward-facing CEB surface to form a melt pool **2** having a given temperature, size and shape, which may have involved a gradual increase in total heat flow and changes in the heat flow profile, the melt pool temperature, size and shape may be maintained substantially constant by regulating the application of the heat source to deliver a substantially constant total heat flow **H** and heat flow profile **P**. The heat flow profile **P** may be maintained substantially constant, and the loss of material from melt pool **2** to the exiting coated core at rate **R** be compensated, by gradually moving the CEB upwards during the coating process, thereby gradually consuming solid CEB portion **1** by introducing material into melt pool **2** at rate **R**. A stable coating process may thus be maintained allowing a significant fraction of the CEB to be melted and applied to a length of core.

In order to further enhance process stability, it may be advantageous to maintain a substantially constant length of the path of the elongated core within the melt

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pool. For example, where the size and shape of the melt pool are constant, maintaining fixed the entry and exit points of the elongated core with respect to the melt pool surface may be sufficient to maintain a constant path length.

- 5 The radial uniformity of the coating thickness may be increased by configuring the core to exit the melt pool surface in a direction substantially close to normal to the melt pool surface. Thus, by configuring the size and shape of the melt pool where the elongated core exits and the direction of the path of the elongated core within the melt pool, a coating with a substantially radially uniform thickness may be
10 produced.

The solid portion of the upward-facing CEB surface may be shaped, either as furnished or by melting or subliming portions of solid material, or by resolidifying molten material, by suitable application of the directed heat source. A lip of solid
15 material surrounding the melt pool may improve process stability, by confining the shape and size of the melt pool and reducing spillage of molten material, thereby allowing a greater fraction of a CEB to be applied as coating. For example, Fig. 2A shows a melt pool bounded by a convex surface **4_M** and convex interface **3** that does not reach the edges of the upward-facing CEB surface. A fraction of
20 solid portion **1**, shown extending between a horizontal plane **3_L** intersecting the deepest portion of melt pool **2** and upward-facing surface region **4_B**, forms a lip **1_L** of solid material surrounding a portion of melt pool **2**. Fig. 2B differs in that lip **1_L** extends above the highest point of melt pool surface **4_M**. and further portions of solid surface **4_S** facing the melt pool have been exposed. The shape of melt pool **2**
25 and lip **1_L** shown in Figs. 2A and 2B is merely illustrative.

The shape of the solid lip surrounding melt pool **2** may be further configured to facilitate entry into or exit from regions of the melt pool surface by the elongated core. Such further configuration of the shape of the lip may be performed by
30 regulating application of the directed heat source to melt or sublime selected lip portions. As shown in the top and side views of Figs. 3A and 3B, the height of one or more portions of lip **1_L** may be reduced to facilitate the entry of uncoated core **5_U** into melt pool **2**, by exposing surface region **4_U**, or the exit of the coated core **5_C**, by exposing surface region **4_C**. If only the lip region on the entry side is
35 lowered, the path of elongated core segment **5_M** within the melt pool may be set

such that the coated core 5_c exits higher than where uncoated core 5_u enters melt pool **2**. Since entry of the uncoated core into the melt pool is less critical to the coating process than exit of the core, where the coating is actually applied, some loss of melt pool material may be accommodated where uncoated core 5_u enters melt pool **2**, while at the same time allowing the exit side of the melt pool to be contained by a lip portion that has not been lowered. A lower entry point into the melt pool of uncoated core 5_u , accompanied by a higher exit point, may enhance access to a region of melt pool surface with a surface normal closer to the direction of motion of the elongated core where coated core 5_c exits melt pool **2**. On the other hand, lip portions on diametrically opposite sides of the melt pool may both be lowered, such that the path of the elongated core may be horizontal, as shown in Fig. 3A.

The coating method and system may be extended to coat the elongated core successively with material from a CEB having a defined composition and from one or more additional CEBs having the defined or other compositions. Fig. 4 shows schematically a method and system for successively applying a coating to uncoated core 5_u from a CEB having the defined composition, including solid portion 1_1 separated from melt pool 2_1 by interface 3_1 , and from a second, i.e., additional, CEB, including solid portion 1_2 separated from melt pool 2_2 by interface 3_2 . Total heat flow H_1 is shown being delivered into heat delivery area 4_{H1} with a heat flow profile indicated by arrows P_1 across surface 4_{M1} of melt pool 2_1 , and total heat flow H_2 is shown being delivered into heat delivery area 4_{H2} with a heat flow profile indicated by arrows P_2 across surface 4_{M2} of second melt pool 2_2 . Heat flows H_1 and H_2 may be delivered from separate directed heat sources or from the same heat source, depending on its capabilities and configuration.

A portion of uncoated core 5_u is shown, propelled at speed V , entering first melt pool 2_1 , a portion 5_{M1} is shown passing through the first melt pool, a portion 5_{C1} is shown emerging from and coated with material the first melt pool 2_1 , and may be optionally cooled and solidified before passing through the second melt pool, shown as portion 5_{C1M2} , before emerging coated with material from the first melt pool and second melt pools, shown as portion 5_{C1C2} . Though not shown in Fig. 4, the core may move in substantially longitudinal directions through melt pools 2_1

and **2₂**, which are neither aligned along the same overall direction nor with the direction of motion between melt pools. Though not shown in Fig. 4, one or more of the upward-facing CEB surfaces may be shaped by regulation of the application of the one or more directed heat sources to form lips of solid material, as shown
5 in Figs. 2 and 3.

The process shown in Fig. 4 may be repeated using more than one additional CEB having the defined composition or having one or more additional defined compositions. In this way a series of coatings, having substantially the defined
10 composition of the first CEB, or having substantially one or more additional defined compositions, may be built up successively around a core. For example, Fig. 5b shows a schematic cross section through a wire, showing a core **5**, first coating **C₁** of uniform radial thickness **T₁**, second coating **C₂** of uniform radial thickness **T₂**, and a third coating **C₃** of uniform radial thickness **T₃**. The coating
15 thickness is shown as radially uniform, which need not be the case.

Where different compositions are used for successive coating layers, some inter diffusion or reaction between the successive coating layers, or even formation of an intermediate reaction layer, may be accommodated, if the structural integrity
20 of the resulting wire is not compromised. In some applications, interdiffusion and reaction between successive coating layers may be advantageous, since it may increase the structural integrity of the wire.

Wires made by the above methods may be used in a range of applications, as
25 components of functional materials, in additive manufacturing, near net-shape manufacturing, and creating wire forms for HIPping. In additive manufacturing, a wire formed from a coated core may be fed towards a work-piece surface, melted using a work-piece-directed heat source and the molten material incorporated into the work-piece surface. Where wires including a core and one or more coatings
30 are used in additive manufacturing, because the core and coating may be melted, the combined composition of the core and the one or more coating layers will govern the composition of the material deposited once the wire is melted and solidified.

A system for conducting the above methods may include: a directed heat source configured to form a melt pool on an upward-facing surface of at least one consolidated elemental block having a defined composition; a core feeder configured to pass a length of elongated core in a substantially longitudinal
5 direction through the melt pool; and, a wire receiver configured to receive the length of wire including an elongated core and multi-elemental coating having substantially the defined composition. The coated core may be passively or actively cooled to form the wire, which may be spooled and stored for later use.

10 If the system is to be used for additive manufacturing, it may further comprise, optionally without intermediate wire spooling and storage, a wire feeder configured to feed the length of wire towards a work-piece surface, a work-piece directed heat source configured to melt the wire as it is fed and incorporate it into a work-piece surface. The work-piece may be mounted on a movable stage to
15 allow or facilitate motion between work-piece directed heat source and work-piece. Advantages of such an integrated system are that wire may be produced as needed and that the wire need not be cooled entirely before application of the work-piece directed heat source, thus reducing the total energy input required.

20 Although the present invention has been described in connection with the specified embodiments, it should not be construed as being in any way limited to the presented examples. The scope of the present invention is set out by the accompanying claim set. In the context of the claims, the terms "comprising" or "comprises" do not exclude other possible elements or steps. Also, the mentioning
25 of references such as "a" or "an" etc. should not be construed as excluding a plurality. The use of reference signs in the claims with respect to elements indicated in the figures shall also not be construed as limiting the scope of the invention. Furthermore, individual features mentioned in different claims, may possibly be advantageously combined, and the mentioning of these features in
30 different claims does not exclude that a combination of features is not possible and advantageous.

CLAIMS

1. A method for producing wire comprising a core and a multi-elemental coating, comprising:
 - 5 furnishing a consolidated elemental block having a defined average elemental composition; FURTHER CHARACTERIZED BY:
 - applying a directed heat source to an upward facing surface of the consolidated elemental block to form a melt pool having substantially the defined average elemental composition;
 - 10 passing a length of elongated heat-resistant core in a substantially longitudinal direction through the melt pool to apply to the length of heat-resistant core a coating comprising material from the melt pool; and,
 - cooling the length of coated core to form a length of wire comprising a core surrounded by a coating having substantially the defined average elemental
 - 15 composition.
 2. The method of claim 1, wherein the elongated heat-resistant core is a filament or strip.
 - 20 3. The method of claims 1 or 2, wherein the directed heat source comprises an electron beam, a laser, a plasma source, or a focused incoherent light source.
 4. The method of any of claims 1 to 3, further comprising applying the coating at a substantially uniform rate by regulating one or both of the melt pool
 - 25 temperature and the speed of passage of the elongated core through the melt pool.
 5. The method of any of claims 1 to 4, further comprising maintaining substantially constant one or more of the temperature, size or shape of the melt
 - 30 pool by regulating application of the directed heat source.
 6. The method of any of claims 1 to 5, further comprising maintaining substantially constant the length of the path of the elongated core within the melt pool.

7. The method of any of claims 1 to 6, further comprising applying the coating with a substantially uniform radial thickness by configuring the elongated core to exit the melt pool substantially close to a surface normal direction.
- 5 8. The method of any of claims 1 to 7, further comprising configuring the shape and size of the melt pool and the shape of a solid portion of the upward-facing surface to form a lip of solid material surrounding the melt pool.
9. The method of claim 8, further comprising configuring a portion of the lip to
10 facilitate entry of the elongated core into the melt pool.
10. The method of claims 8 or 9, further comprising configuring a portion of the lip to facilitate exit of the coated elongated core from the melt pool.
- 15 11. The method of any of claims 1 to 10, further comprising:
furnishing one or more additional CEBs;
applying the directed heat source and/or one or more additional directed heat sources to each of one or more upward-facing surfaces of each of the one or more additional CEBs to form one or more melt pools;
20 passing the at least a fraction of the length of coated core in a substantially longitudinal direction successively through each of the one or more melt pools to apply one or more successive coatings comprising material from the one or more melt pools; and,
cooling the length of twice or more coated core to form a length of wire
25 comprising a core surrounded by a coating having substantially the defined composition and one or more additional coatings.
12. The method of claim 11, wherein the additional CEBs have the defined composition or one or more additional defined compositions.
- 30 13. The method of any of claims 1 to 12, further comprising using at least a fraction of the length of wire in additive manufacturing by feeding the at least a fraction of the length of wire towards a work-piece surface, applying a work-piece-directed heat source to melt the at least a fraction of the length of wire and

incorporating the molten at least a fraction of the length of wire into the work-piece surface.

14. A system for forming a wire according to the method of any of claims 1 to 5 12, comprising:

a directed heat source configured to form a melt pool on an upward-facing surface of a consolidated elemental block having a defined composition; and

a core feeder configured to pass a length of elongated core in a substantially longitudinal direction through the melt pool and apply a coating 10 having substantially the defined composition to the length of elongated core; and

a wire receiver configured to receive a length of wire comprising the elongated core and multi-elemental coating having substantially the defined composition.

15 15. The system of claim 14, further comprising a work-piece-directed heat source, a wire feeder and a work-piece mounting stage, configured to use at least a fraction of the length of wire in additive manufacturing according to the method of claim 13.

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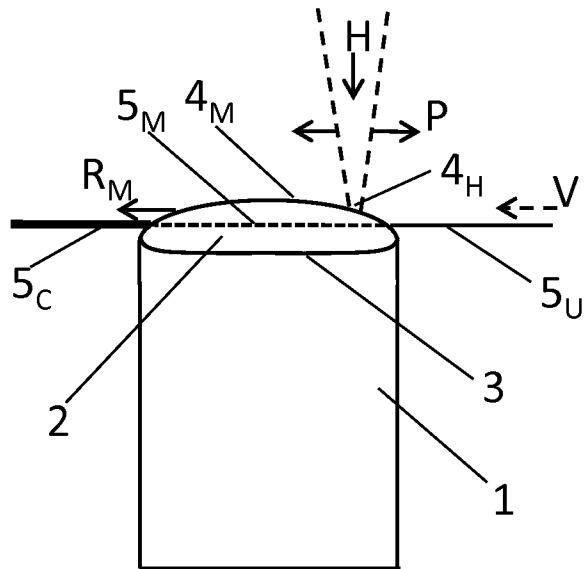


FIG. 1

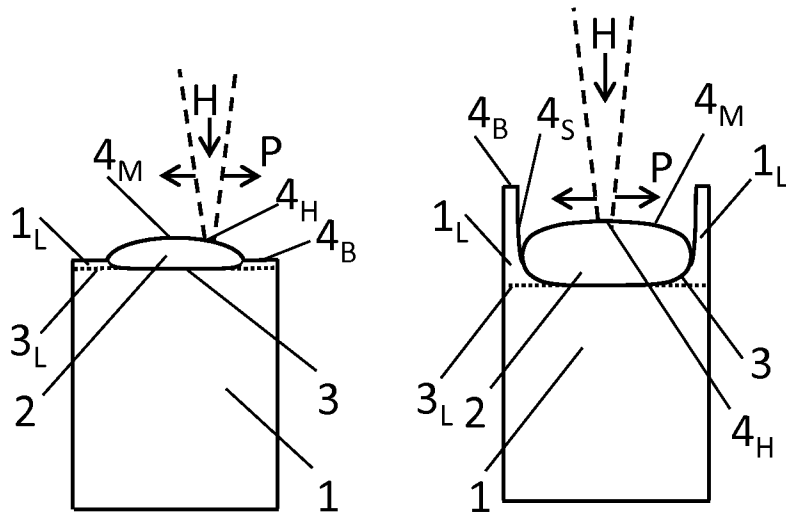


FIG. 2A

FIG. 2B

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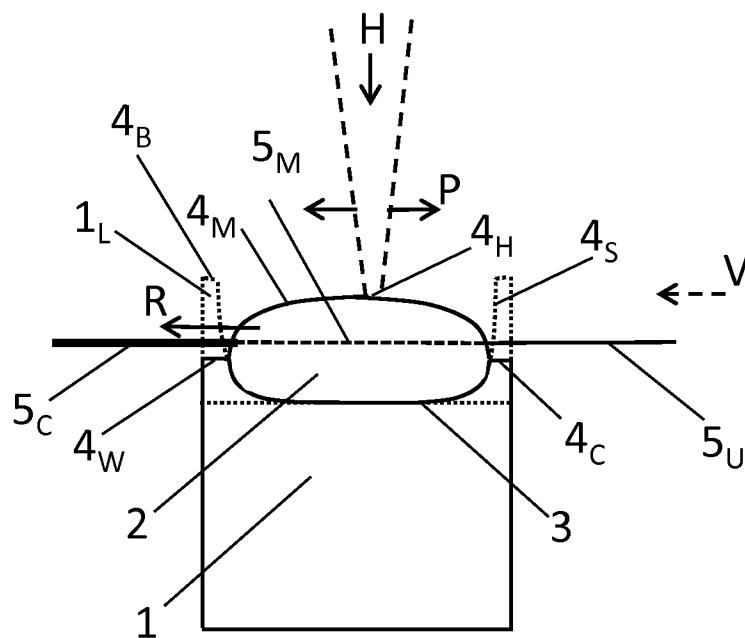


FIG. 3A

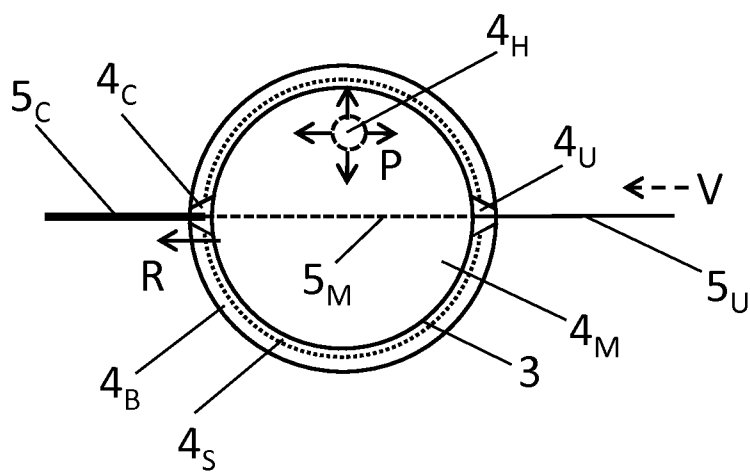


FIG. 3B

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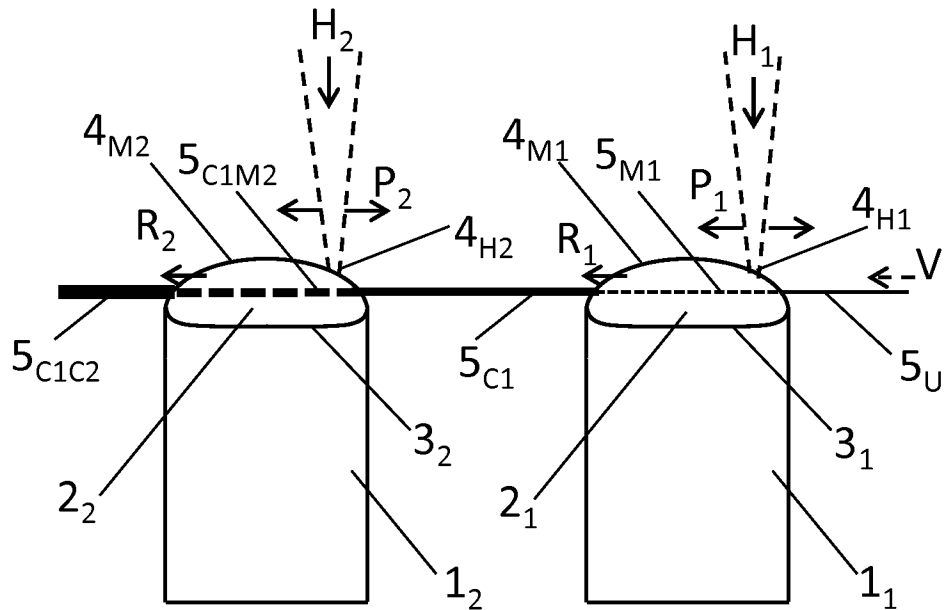


FIG. 4

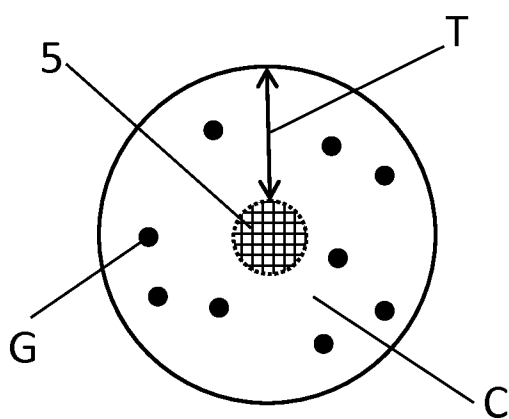


FIG. 5A

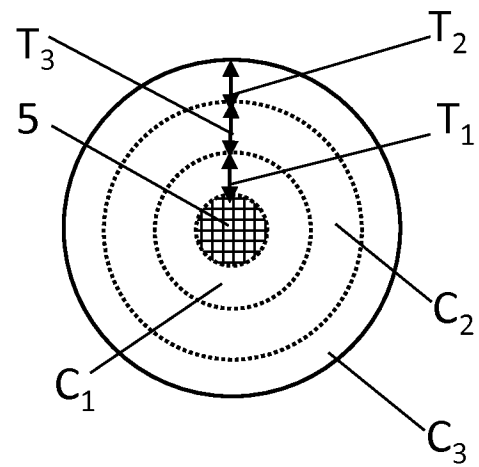


FIG. 5B

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/066176

A. CLASSIFICATION OF SUBJECT MATTER
INV. C23C2/00 C23C2/38 C23C26/02
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

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, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 626 826 A (GLACIER CO LTD; ALFRED LEATHERS) 21 July 1949 (1949-07-21)	1,2,4-15
Y	page 4, line 29 - line 128; claim 1; figure 1	3
X	JP H01 290753 A (NIPPON TELEGRAPH & TELEPHONE) 22 November 1989 (1989-11-22)	14,15
Y	abstract; figure 1	3
A	US 5 662 969 A (LING PING [AU]) 2 September 1997 (1997-09-02) cited in the application column 2, line 65 - column 4, line 38; figures 1,4	1-15
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

"&" document member of the same patent family

Date of the actual completion of the international search

10 April 2014

Date of mailing of the international search report

22/04/2014

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2013/066176

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 174 570 B1 (DAMBRINE BRUNO JACQUES GERARD [FR] ET AL) 16 January 2001 (2001-01-16) cited in the application claims 1-13; figures 1-3 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/066176

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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