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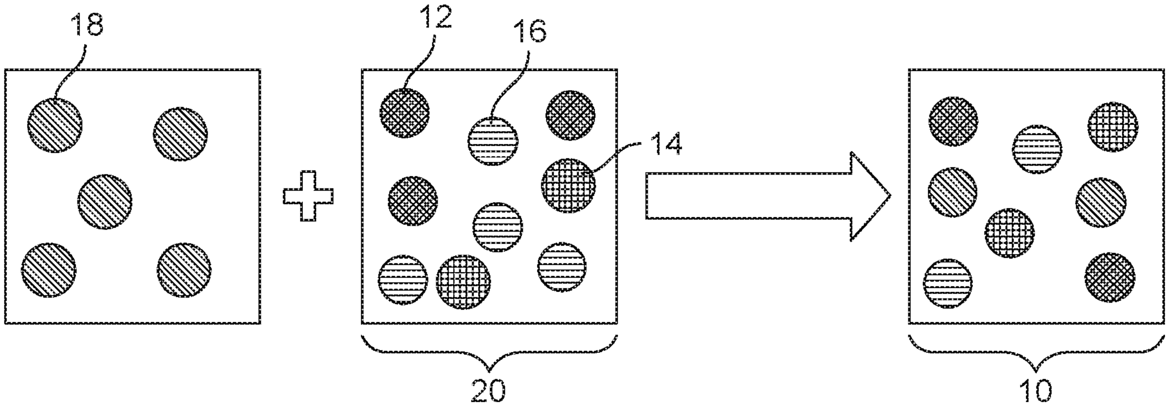

FIG. 1

06 12 19

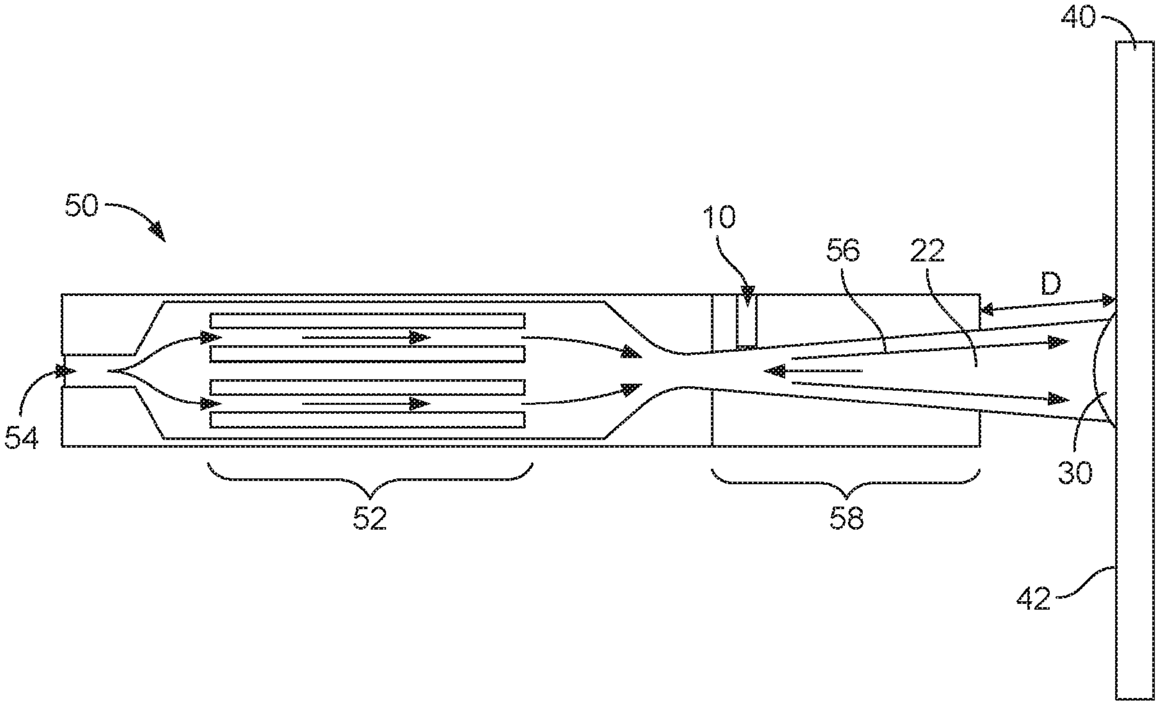

FIG. 2

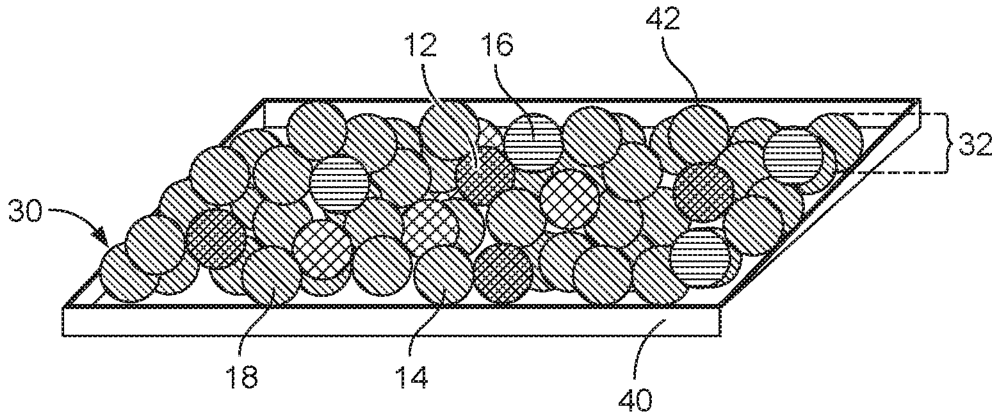

FIG. 3

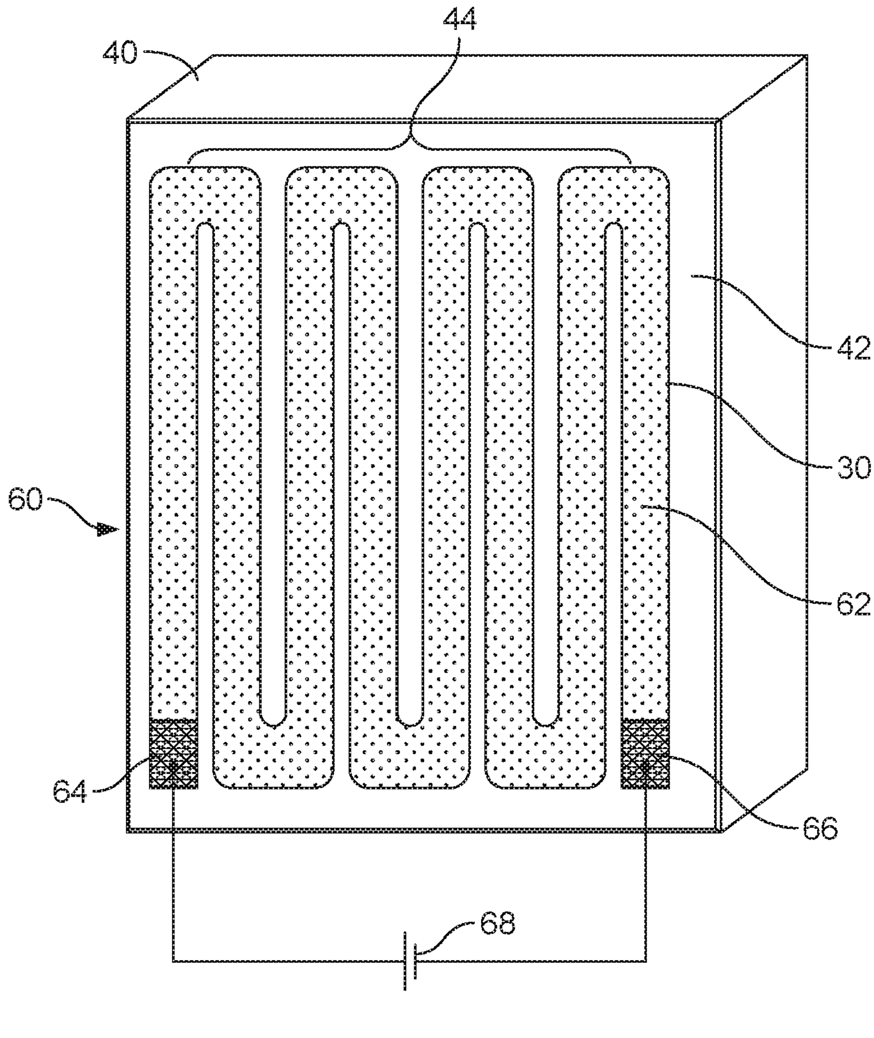

FIG. 4

The following terms are registered trade marks and should be read as such wherever they occur in this document:

Polyvision
Inconel

A HEATING DEVICE, AND APPLICATIONS THEREFORE

[0001] This invention relates to a heating device and applications therefore.

[0002] More particularly it relates to a novel heating device comprising a heating element comprising an ohmically resistive coating, and the low-cost manufacture thereof. The method deposits a novel blend of particles onto a substrate using what is referred to in the art as a “cold spray” or “solid-state” deposition technique.

[0003] The heating element can then be electrically powered, with an AC or DC source, to ohmically heat the coating in question.

BACKGROUND

[0004] Various techniques are known for producing surface coating heating elements using deposition techniques which heat one or more metals and /or oxides, carbides, silicides, di-silicides, nitrides, borides, and sulphides to a sufficiently high temperature, typically above 3,000ºC, to enable the deposition process to take place via a semi-molten phase. Such a process, due to the high operating temperatures, places limitations on the substrate, and has cost implications, making the production of goods for many applications restrictively expensive.

[0005] These semi-molten phase applications, that use either powdered or wire fed feed-stocks, include inter alia flame-spraying using a range of oxy-fuel combustion gases, high velocity oxy-fuel techniques (HVOF) and plasma spraying devices, each operating at progressively higher operating temperatures and/or kinetic energy inputs. These techniques are well established commercially, but, have limitations in their applications, notably because, being high temperature applications, problems can arise from the uncontrolled release of in-built stresses in the substrate from the manufacturing process. This can lead to instability and distortion, particularly where larger surface lengths and or areas, namely ones of a magnitude of one square metre or more, are concerned, especially where the substrate is thin. Established custom and practice is to cool such sensitive substrates during the high temperature spraying process using water cooled platens, dry-ice baths, or the like, to cool the article being sprayed. Such measures are not always feasible or add complexity to the deposition process. In consequence productivity and production cost can both be negatively impacted, whilst the risk of producing poor quality articles is increased.

[0006] In PCT/GB2005/003949, PCT/GB2007/004999 and PCT/GB2009/050643 the applicant has described the production of electrical heating elements using flame spraying techniques. Whilst intended for the manufacture of various articles e.g. domestic white goods, commercial cooking appliances and big-science applications using Ultra-High Vacuum installations, the applicant has identified considerable new market opportunities, based on, for example, the application of ultra-slim surface coating heating elements onto, particularly, high grade architectural panels, comprising a mild steel core with a thin ceramic coating on one or both surfaces, such coating possessing high dielectric resistance strength, even when heated under appropriate electrical load to high temperatures, such as 400°C.

[0007] Current considered wisdom is that brittle or hard metal compounds can’t be deposited on a substrate by any means other than semi-molten phase applications, because the compounds, being abrasive in nature, would otherwise destroy the surface on which they would be deposited.

[0008] Applicant has, surprisingly, determined that it is possible to deposit such brittle or hard metal compounds, including those typically commercialised powder particles used in current thermal spraying applications, at what are considered lower temperatures in the context of spray deposition, by depositing the brittle or hard metal compounds together with a ductile or malleable metal or metals.

[0009] Applying these metal compounds to the surface of substrates enables the production of heating devices which can be used in a variety of applications including for space heating purposes in, for example, domestic, commercial and industrial premises.

[0010] An ideal substrate for such applications are architectural panels comprising a steel core with a thin ceramic coating, such as those obtained from Polyvision® BV, such as their Polyvision® Flex 1 or Flex 2 panels.

[0011] Preferred coatings include those produced from blending nickel oxide and zinc, though many other combinations have been successfully demonstrated.

[0012] Other heating applications include automotive applications, particularly in the electric and hybrid power-train fields for low wattage cabin heating appliances, aerospace applications for anti-icing and/or de-icing purposes, and construction industry applications, with the coatings being onto cementitious and other building materials.

[0013] Cited art addressed in prosecution included:

[0014] W02016/084019 which utilises thermal spay techniques which melt the powders they deposit.

[0015] W02014/184146 which teaches cold spraying of metals.

[0016] US3922386 which discloses a heating element produced by theremal spraying.

[0017] GB2344042 which discloses a method of producing resistive heating elements by heating previously oxidized particles.

[0018] WO2005/079209 which discloses the production of nano layers.

[0019] US2018/0138494 which discloses depositing cathode or anode materials using a cold spray process and CN107841744 which discloses the use of cold spray to produce ceramic doped metal based composites.

BRIEF SUMMARY OF THE DISCLOSURE

[0020] In accordance with a first aspect of the present inventions there is provided a heating device (60) comprising a substrate (40) with a surface (42) having a heating element (62) comprising an ohmically resistive coating (30) which has been deposited on the surface (42) of the substrate (40) by cold spray or solid state deposition, the ohmically resistive coating has a layer (32) thickness of between 2 and 300 microns and comprises:

i) 40-60% by weight of one or more ductile or malleable metals (18) selected from: copper, aluminium, zinc, and manganese; and

ii) electrically resistive particles (20) comprising compounds or salts (16) of metals (12) and or metalloids (14);

wherein the one or more ductile or malleable metals (18) bond the electrically resistive particles (20) to the surface (42) of the substrate (40) to form the ohmically resistive coating (30) as a consequence of the cold spray or solid state deposition operating at a temperature (T) below a melting temperature of the one or more ductile or malleable metals (18), and

at least a pair of electrical contacts (64; 66) disposed thereon for connection to an AC or DC power supply (68).

[0021] The heating device is produced from a blend, by cold spray or solid-state deposition, comprising:

i) at least one ductile or malleable metal, together with

ii) particles comprising either of:

a) one or more metals and/or one or more metalloids together with compounds thereof; or

b) one or more metal or metalloid compounds;

the at least one ductile or malleable metals being present in an amount, by weight, sufficient to allow the blend to form a coating on a surface of a substrate when deposited at temperatures below 1,000°C.

[0022] Preferably the one or more metal or metalloid compounds comprise one or more of an oxide, carbide, silicide, di-silicide, nitride, boride, or sulphide.

[0023] Most preferably the one or more metal or metalloid compounds is an oxide.

[0024] Preferably the one or more metal compound comprises: copper, gold, lead, aluminium, platinum, nickel, zinc, chromium, magnesium, iron, manganese, titanium, vanadium, niobium, indium, terbium, strontium, cerium, and lutetium.

[0025] Most preferably the one or more metal compound comprises nickel.

[0026] Preferably the one or more metalloid is selected from: boron, silicon, germanium, arsenic, antimony, tellurium and astatine.

[0027] Preferably the one or more ductile or malleable metal is selected from: gold, silver, aluminium, copper, tin, lead, zinc, iron, manganese, platinum, nickel, tungsten and magnesium.

[0028] Most preferably the one or more ductile or malleable metal is zinc or zinc in admixture with nickel.

[0029] The blend may comprise, by weight, from 10 to 90% of one or more ductile or malleable metals.

[0030] Most preferably the blend comprises from 40 to 60% of one or more ductile or malleable metals.

[0031] Typically, the particles comprising either of:

a) one or more metals and/or one or more metalloids together with compounds thereof; or

b) one or more metal or metalloid compounds

have a mean particle size of 0.1-150 microns.

[0032] Most preferably the particles have a mean particle size of from 5-35 microns.

[0033] In a particularly favoured embodiment the particles comprise oxides of nickel, iron and/ or chromium.

[0034] The one or more metals and/or one or more metalloids together with compounds thereof may be obtained as, for example, pre-oxidised (or other) powders obtained by passing metal powders through a heating zone of a thermal deposition apparatus under an air atmosphere (or other appropriate gas) such that the metal powders become molten and oxidise (or other) to a controllable degree prior to being quenched, isolated and dried.

[0035] The electrically resistive metal oxides (carbide, silicide, di-silicide, nitride, boride, sulphide and other non-metal and/or metalloid or any combination of such) and admixtures of the same are preferably selected from those which exhibit an increase in resistance with increasing temperature.

[0036] The blend is used to form a coating comprising a layer formed from a blend which has been deposited on a surface of a substrate.

[0037] Preferably the layer has a thickness of between 2 and 300 microns.

[0038] Most preferably the layer has a thickness of between 20-70 microns.

[0039] Preferably the layer covers at least 10%, by area, of the surface of the substrate.

[0040] Most preferably the layer covers at least 50%, by area, of the surface of the substrate.

[0041] The layer may be deposited as single or multiple, separated or overlapping, track(s).

[0042] The coating can be deposited in a manner such that it can have constant dimensions (uniform width and thickness) or can be deposited in a variable manner such that the resistance (and consequential heating effect) at a given point or area can be controlled so that non-uniform effects can be achieved if desired. This can be done by changing the track's shape or configuration, for example, by altering the width or thickness of the deposit, and / or by changing the formulation and/or level of metal compound, particularly metal oxide present, or by changing the spacing between adjacent tracks. In this manner, it is, for example, possible to achieve greater heating effects, at the periphery of a structure compared to say it's centre or to provide separately controllable heating zones within a larger heater surface such that, when connected via an intelligent central control unit, a tuneable heating output can be obtained. A tuneable system can accommodate seasonal heating variations or provide improved energy efficiency during routine usage.

The blend may be deposited in a method comprising depositing

i) at least one ductile or malleable metal together with

ii) particles comprising either of:

a) one or more metals and/or one or more metalloids together with compounds thereof; or

b) one or more metal or metalloid compounds;

to form a coating on a surface of a substrate

comprising the steps of causing the blend to adhere to the surface by:

i) feeding blend components into a cold spray apparatus; and

ii) depositing blend particles via a heated, compressed, supersonic gas jet which accelerates the blend particles through a nozzle, at a temperature and pressure to the surface of the substrate which is positioned a distance from the nozzle, such that the blend particles adhere to the surface, forming a coating thereon.

[0043] The temperature may be between 100°C and 1,200°C.

[0044] Most preferably the temperature is below 600°C.

[0045] More preferably still the temperature is below a temperature that would cause the melting or partial softening of the one or more ductile or malleable metal particles.

[0046] Preferably the pressure is between 1 and 10 Atm (101,325 to 1,013,250 Pa).

[0047] Preferably the method is conducted absent of a vacuum.

[0048] Preferably the distance is less than 1m, more preferably still between 1 and 30 cm.

[0049] Preferably the particles have a mean particle size of 0.1 to 150 microns, more preferably 15 to 35 microns.

[0050] Preferably the gas is air, oxygen, nitrogen, carbon dioxide, argon or neon, although other gases used in, for example, welding might be used.

[0051] The heating device of the invention comprises a substrate with a surface having a heating element comprising a coating and at least a pair of electrical contacts disposed thereon which heating element, in operation, is connected to an AC or DC power supply.

[0052] Preferably the heating device comprises a plurality of heating elements each sharing a common feed terminal and having an independent return terminal.

[0053] The heating element may be connected to the AC or DC power supply by mechanical means, soldering, laser brazing and laser welding, additive manufacturing solid state deposition of ductile metals or by the use of electrically conductive adhesives or inks. The connections can be made at the respective ends and additionally at intermediate points along its length.

[0054] In one mode of operation the power supply is mains operated.

[0055] In a preferred mode of operation, the power supply is a low voltage supply operating in the range of 1 to 110 Volts, more preferably still below 30 Volts.

[0056] Preferably the substrate surface comprises a dielectric barrier material.

[0057] In a particularly favoured embodiment the dielectric barrier material comprises a ceramic.

[0058] Preferably the substrate comprises a sheet material, most preferably an architectural panel.

[0059] The sheet material may comprise a steel core and a ceramic surface.

[0060] Alternatively, the sheet material may comprise ceramic, glass or mirrored glass.

[0061] The sheet may vary in size and comprise a heated surface area of between 150cm^2 and 20,000cm^2.

[0062] Preferably the heating element is a self-regulating resistance heating element.

[0063] The coating may also be “protected” by overlaying it with a protective layer. The protective layer may take the form of, for example, a film, a sheet, a coating, or an applied screed which may protect against wear, or penetration by e.g. water or substances corrosive to the heating element and to provide a degree of protection against accidental contact with such hot surfaces, or to protect against electric shock from accidental contact with an electrically live element.

[0064] Additionally, the protective/additional layer may be used to make cleaning easier being a low effort wipe-able surface and/or a thermal management coating.

[0065] In a particularly favoured embodiment, there is provided a vehicle comprising a heating element of the fourth aspect of the present invention.

[0066] In another particularly favoured embodiment, there is provided a building comprising a heating element of the fourth aspect of the present invention.

[0067] The heating device can be used to generate local heat or to provide protection from the cold.

[0068] Examples include, by way of illustration only:

- Horizontal and vertical building structures, including all manner of domestic dwellings, including social housing, commercial buildings including offices, shops and retail centres, sporting complexes and industrial premises including logistics centres, workshops and the like;
- Bridges, tunnels, covered walk-ways, bus and train stations, shelters and the like and designated external smoking areas;

- Aircraft external panels or internal panels prone to exposure to low temperatures;
- Railway tracks, more specifically points;
- Stadium terracing and steps, runways, forecourts, roads and walkways;
- Signs and advertising hoardings;
- Industrial cold rooms and freezers; and
- Carwashes, factories, airports, stables, farm and animal stock buildings, stadia, distribution, exhibition, and entertainment centres/complexes, warehouses and other large area/volume buildings.

[0069] Examples of building structures include, by way of example only:

- Walls;
- Ceilings;
- Support columns;
- Floors;
- Roofs (undersides and exposed surfaces-to prevent snow/weight build-up), and
- Functional heat generating units within the structures, including saunas, hot rooms, pizza and tandori ovens.

[0070] The structure may be made of many different materials. Preferred materials which may be treated include, building materials, such as, for example:

- Cementitious, ceramic and like materials, including concrete;
- Asphalt, bitumen and like oil based materials;
- Plastics and polymers;
- Composite materials; and
- Metals, insulated metal surfaces and enamel.

[0071] In accordance with a second aspect of the present inventions there is provided a method of heating a space comprising supplying power to a heating device according to the invention.

[0072] Preferably the method of heating a space heats the coating to >90°C in under 5 minutes.

[0073] Preferably the heat generated is primarily in the form of infra-red radiant heat energy.

[0074] Heat output can, to some degree, be controlled by track configuration. The tracks may be deposited in series, or parallel, or series parallel so as to generate an electrical resistance required to produce the desired heating output per unit area. Examples include:

[0075] For IR radiant room heaters, say, typically 400-800 Watts per m^2,

[0076] For walk ways, signs, terracing, say, typically 200-300 Watts per m^2,

[0077] For building structures, say, typically 40-100 Watts per m^2,

[0078] For aircraft wings, say, typically 100-200 Watts per m^2, and

[0079] For electric vehicle cab heaters say, typically 400-800 Watts per m^2.

BRIEF DESCRIPTION OF THE DRAWINGS

[0080] Embodiments of the invention are further described hereinafter with reference to the accompanying drawings, in which:

Fig 1 is a diagrammatic representation of a blend formed from at least one ductile or malleable metal, together with particles comprising either of:

a) one or more metals and/or one or more metalloids together with compounds thereof; or

b) one or more metal or metalloid compounds;

Fig 2 illustrates an apparatus suitable for use in the method of the third aspect of the invention;

Fig 3; is a diagrammatic representation of a coating of the invention deposited on a substrate; and

Fig 4 illustrates a heating device according to a fourth aspect of the invention.

DETAILED DESCRIPTION

[0081] Referring to Fig 1 there is illustrated a blend (10), for cold spray or solid-state deposition, produced by mixing i) at least one ductile or malleable metal (18), typically as particles, with ii) particles (20) comprising a) one or more metals (12) and /or metalloids (14) together with compounds thereof (16) or b) one or more metal or metalloid compounds (16).

[0082] The blends (10) may be pre-mixed and introduced into a cold spay or other solid-state deposition apparatus for use in the method of the invention or may be introduced separately and mixed in situ.

[0083] Referring to Fig 2, the blend (10) may be fed into a cold spray apparatus (50) such that blend particles (22) pass into a heated (52), compressed (54), supersonic gas jet (56) where they are accelerated through a nozzle (58) at a temperature (T) and pressure

(P) to the surface (42) of a substrate (40) which is positioned a distance (D) from the nozzle such that the blend particles (22) adhere to the surface (42) forming a coating (30).

[0084] The result is a coating (30), see Fig 3, in which the i) at least one ductile or malleable metal (18) serves to “bond” ii) particles (20) comprising a) one or more metals (12) and /or metalloids (14) together with compounds thereof (16) or b) one or more metal or metalloid compounds (16) to the surface (42) of the substrate (40).

[0085] In an exemplary method the blend (10) may be as illustrated in any of Examples 1 to 7.

[0086] Particles having a mean diameter of 5 to 35 microns are heated in a gas stream of air, to a temperature of below 600 C, and at a pressure of about 5 Atm (506625 Pa) where they leave the apparatus and travel a distance of between 8mm- 300mm where they are deposited on a ceramic surface (42) where they form a coating (30) in a layer (32) with a thickness of about 45 microns.

[0087] The coating (30) may be deposited in a controlled manner forming a track or tracks (44) which may form, for example, a functional component. Thus, as illustrated in Fig 4, a heating device (60) comprises a steel substrate (40) with a ceramic surface (42) onto which has been deposited, in a tracked manner, a heating element (62) comprising, for example, a coating (30) comprising nickel oxide and zinc. A pair of electrical contacts (64; 66) is provided which can be connected to a power source (68) such that the heating device can be heated.

[0088] Alternatively, the arrangement may comprise a plurality of heating elements sharing a common feed terminal (64) and having independent return terminals (66).

[0089] The power source is preferably a low voltage supply of less than 30 V.

[0090] The heating device may be used in many different applications, but two particularly favoured applications are in vehicles such as, but not limited to, cars, lorries, trains, boats and airplanes and in buildings such as, but not limited to: houses, offices, hospitals, and warehousing.

[0091] To further exemplify the invention(s) there follow some exemplary blends, and details of their deposition onto substrates to form heating elements.

Example 1

[0092] A blend (10) of zinc metal powder (18), nickel metal powder (12) and alumina (16) powder in a mix, by weight, of 75:23:2 and with a particle size range of between 15 and 30 μm was deposited using a cold spray or solid state apparatus, at 10mm separation onto a vitreous enamelled (42) steel substrate (40), using compressed air at 5.6bar (560,000 Pa) as the carrier gas, heated at ~600°C, as deposited parallel element tracks of some 0.45cm width with a spray speed of 4 cm/sec. When a 20V AC power supply was connected across the length of the deposited element track, the latter heated to 120°C, drawing 4 amps of current.

Example 2

[0093] The same blend of zinc powder, nickel powder, and alumina, as used in Example 1, was blended 1:1 with a thermally pre-oxidised Inconel® 600 alloy (to around 10% overall oxidation level and 45μm to dust) at 5.6 bar (560,000 Pa) pressure and were deposited using a 12mm separation and 4cps spraying speed onto a plasma sprayed alumina steel substrate, using compressed air as the carrier gas, heated at ~600°C, as deposited adjacent tracks to a total width of ~4.5cm. When a 10V AC power supply was connected across the length of the deposited element track, the latter heated to 60°C, drawing 3 amps of current.

Example 3

[0094] A blend as per Example 2 was sprayed at 400°C onto a toughened glass substrate using a 10cm separation and an 8cps traverse speed and deposited as parallel elements of some 0.45cm width.

Example 4

[0095] A blend as in Example 2 was sprayed onto a SiN ceramic block at 600°C and 5.6 bar (560,000 Pa) pressure, using an 8 cm separation and 4cps traverse speed, producing adjacent tracks to a total width of ~4.5cm.

Example 5

[0096] A 4:1 blend of nickel oxide powder (16) (15μm) with zinc metal powder (18) at 600°C and 4.4 bar (440,000 Pa) pressure, using an 8 cm separation and 8cps traverse speed, was sprayed onto a ceramic coated steel architectural panel, depositing parallel element tracks some 0.45cm wide.

Example 6

[0097] A blend of zinc metal powder (18), nickel metal powder (12) and thermally pre-oxidised Inconel® 600 alloy (16) as used in Example 2 was sprayed onto a ceramic coated steel architectural panel at 400°C and 5.6 bar (560,000 Pa) pressure, using an 8 cm separation and 12 cps traverse speed, depositing parallel element tracks some 0.45cm wide. When a 40V DC power supply was connected across the length of the deposited element track, the latter heated to 110°C, drawing 2 amps of current.

Example 7

[0098] A 6:1 blend of a thermally pre-oxidised Inconel® 600 alloy (16) as used in Example 2 and zinc metal powder (18) was sprayed onto a ceramic coated steel architectural panel at 570°C and 5.6 bar (560,000 Pa) pressure, using an 8 cm separation and 4 cps traverse speed, depositing parallel element tracks some 0.45cm wide. When a 240V AC mains power supply was connected across the length of the deposited track, the latter heated to 250°C, drawing 0.9 amps of current.

CLAIMS

1. A heating device (60) comprising a substrate (40) with a surface (42) having a heating element (62) comprising an ohmically resistive coating (30) which has been deposited on the surface (42) of the substrate (40) by cold spray or solid-state deposition, the ohmically resistive coating has a layer (32) thickness of between 2 and 300 microns and comprises:

i) 40-60% by weight of one or more ductile or malleable metals (18) selected from: copper, aluminium, zinc, and manganese; and

ii) electrically resistive particles (20) comprising compounds or salts (16) of metals (12) and or metalloids (14);

wherein the one or more ductile or malleable metals (18) bond the electrically resistive particles (20) to the surface (42) of the substrate (40) to form the ohmically resistive coating (30) as a consequence of the cold spray or solid-state deposition operating at a temperature (T) below a melting temperature of the one or more ductile or malleable metals (18), and

at least a pair of electrical contacts (64; 66) disposed thereon for connection to an AC or DC power supply (68).

2. A heating device as claimed in claim 1 wherein in ii) the compounds or salts are selected from an oxide, carbide, nitride, boride, silicide or di silicide.

3. A heating device as claimed in claim 1 or 2 wherein the device comprises a plurality of heating elements (62) each sharing a common feed terminal (64) and having an independent return terminal (66).

4. A heating device as claimed in any or claims 1 to 3 in which the power supply is mains operated.

5. A heating device as claimed in any of claims 1 to 3 wherein the power supply is a low voltage supply operating in the range of 1 to 110 Volts.

6. A heating device as claimed in claim 5 wherein the power supply is a low voltage supply operating below 30 Volts.

7. A heating device as claimed in any of claims 1 to 6 wherein the surface (42) comprises a dielectric barrier material.

8. A heating device as claimed in claim 7 wherein the dielectric barrier material is a ceramic.

9. A heating device as claimed in any of claims 1 to 6 wherein the substrate (40) comprises a sheet material.

10. A heating device as claimed in claim 9 wherein the sheet material is an architectural panel.

11. A heating device as claimed in claim 9 or 10 wherein the sheet material comprises a steel core and a ceramic surface.

12. A heating device as claimed in claim 9 wherein the sheet material is a glass or mirrored glass sheet.

13. A heating device as claimed in any of claims 1 to 12 wherein the surface has a heated surface area of between 150cm^2 and 20,000cm^2.

14. A heating device as claimed in any of claims 1 to 13 wherein the heating element is a self-regulating resistance heating element.

15. A vehicle comprising a heating element as claimed in any of claims 1 to 14.

16. A building comprising a heating element as claimed in any of claims 1 to 14.

17. A method of heating a space (70) comprising supplying power to a heating device (60) as claimed in any of claims 1 to 14.

18. A method of heating a space as claimed in claim 17 which heats the heating device to >90°C in under 5 minutes.

19. A method of heating a space as claimed in claim 17 or 18 wherein the heat generated is primarily in the form of infra-red radiant heat energy.