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(54) Title: SPRAY DEPOSITION

(57) Abstract

A method of spray deposition in which an addition or reactant material is deliberately added for diffusion or reaction with a base material being atomised. The addition may be particles of a different metal, metal alloy, ceramic or a non-metallic material introduced into the stream or spray to form an alloying addition to the base material producing an alloy whose composition prevents successful production by conventional or powder metallurgic technology. Alternatively the addition may reduce by reaction the porosity in a forming deposit which would otherwise be present. In such a case the addition may be a reactive gas added to the atomising gas or a reactive material deliberately added to the base material to react with entrapped atomising gas. A reaction can also be initiated to cause evolution of a gas so that porous or foamed metal can be produced.

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SPRAY DEPOSITION

This invention relates to the spray deposition of a molten metal, metal alloy or non-metal in which a stream of molten metal, metal alloy or non-metal e.g. ceramic is atomised into droplets by high velocity atomising gas at a temperature less than the molten stream.

In the spray deposition of molten metal or metal alloy the atomising gas used is normally either nitrogen or argon. However, in a spray deposition process, the porosity of the deposit varies according to the atomising gas used and the metal or metal alloy being atomised. For example, the article "Spray Forming" constituting report number 85CRD073 of May 1985 of General Electric reported on an evaluation of disc preforms of Rene 80. Atomisation was conducted with both argon and nitrogen and respective densities of 99.4% and 99.9% were measured. The lower density of the argon sprayed preforms was found to be due to argon bubbles being trapped within the deposit causing porosity. Similar porosity was not found in the preforms made by atomising with nitrogen atomising gas because of a reaction between the nitrogen gas and nitride forming elements in the alloy. However, not all metals act in the same way and, for example, atomisation of copper using nitrogen invariably will result in a deposit having large pores leaving 1 to 4% porosity.

Also in the production of certain alloys it is often the case that the alloying is limited by macrosegregation during solidification or, in the case of powder metallurgy, by precipitation in the teeming nozzle during atomisation. For example, in an ingot route only a limited addition of aluminium can be added to stainless steel due to subsequent segregation problems during solidification and oxidation problems leading to formation of large oxides in the melt. In addition, if an attempt is made to overcome these problems by using powder metallurgy and atomising the alloy constituents from a metal then precipitates (e.g. aluminium oxide and nitride) form in the pour nozzle restricting flow and causing blockage.

An object of the present invention is to provide an improved method of spray deposition. In the preferred aspect the object is making improved and new alloys.

According to the present invention there is provided a method of spray deposition comprising the steps of:

teeming a stream of molten metal or metal alloy or non-metal base material through an atomising device,

directing atomising gas at a temperature less than that of the liquid stream to break up the stream of the base material into a spray of atomised droplets, and applying an addition or a reactant material which is deliberately added for at least one of: reaction with the base material, reaction with the atomising gas, diffusion within the base material, and evolution of a gaseous phase within the base material.

More particularly, according to one aspect of the present invention there is provided a method of producing an alloy by spray deposition comprising the steps of atomising a stream of molten metal particles by subjecting the stream to atomising gas directed at the stream, and introducing into the spray of atomised or atomising particles of the base material, or into the molten stream just prior to atomising, solid or molten particles of a different metal, metal alloy, ceramic or a non-metallic material to form an alloying addition to the base material and co-depositing the particles of the base material and the alloying material under controlled conditions such that the deposit formed comprises an alloy of the base material and the alloying addition. Partial or complete alloying can occur on deposition or on subsequent cooling or may be finally completed by diffusion during subsequent heat treatment or hot working. The injection of particles composed of metals of a low atomic number can be particularly beneficial as diffusion can occur very rapidly.

The invention also provides a method of injecting into the spray of atomised particles of a base alloy, solid or molten particles of a metal alloy, ceramic or non-metallic compound which during flight or subsequently on or after deposition, reacts with the base alloy to form a dispersoid composed of constituents from both the base alloy and the injected solid or molten particles.

By this aspect of the invention a spray deposit of an alloy is formed where the alloy has been formed by the co-deposition of atomised particles of a base material and applied particles of an alloying addition or a reactant.

In a preferred method the alloying addition particles are suitably applied by generating a fluidised bed of particles in a gas stream from the bed into the spray so that the alloying addition particles are co-deposited with the atomised base material particles. However, other techniques can be used including screw feeding. Liquid metals can be added to the main spray using a second spraying device arranging the relative atomising rakes to provide the required volume of weight fraction of alloying or reactant addition.

According to another particular aspect of the present invention there is provided a method of forming a deposit from gas atomised metal or metal alloy comprising doping the metal or metal alloy and/or the atomising gas with a material which will react on deposition to reduce the porosity in the deposit which would otherwise have been present without the addition of said material. For example, this aspect of the invention envisages deliberately adding reactive gas to the atomisinng gas and/or deliberately adding a reactive element to the alloy to form a constituent which would not normally be acceptable in conventional forming techniques due to segregation problems but which, in the rapid solidification of an atomising process, improves the density and/or the microstructure of the deposit.

It will be understood that the deposit formed in accordance with the method of the invention may be of any shape, for example bar, strip, plate, disc, tube or intricately shaped articles or may be a coating. It may also be used in the as deposited form or subsequently hot or cold worked or thixotropically formed. The reaction product formed in the deposit need not be solid. Co-depositing a thermally unstable particle with the base metal so that the particle vapourises when entrapped by the depositing metal droplets will form a "foamed" metal structure. The particle or the product of a reaction between the particle and the matrix would be a material that vapourises or decomposes to gas in the matrix. For example, pre-expanded polystyrene beads may be used. These are readily available as particles of about 0.1 mm in size. The extent and size of the porosity could be controlled by adjusting the liquid content of the depositing metal and the volume fraction and size of the injected particles.

Where the applied addition is solid and particulate so as to be co-deposited with the base material it is very important that the heat extraction is carefully controlled by control of the atomising conditions and the temperature and rate of injection of the applied particles. For example an atomised spray will typically have a range of droplet sizes (e.g. 10-300 microns, approximating to a log-normal size distribution) and these arrive at different temperatures and states of solidification at the collector surface. For a given alloy and atomising gas, the cooling rate in flight is mainly determined by the size of an individual particle. Under optimum conditions, the coarse particle (e.g. 300 micron) are deposited in the fully molten condition, the fine particles (e.g. 10 microns) will be deposited fully solidified at a temperature close to that of the atomising gas, and the majority of particles of an intermediate size will be deposited in the semi-solid/semi-liquid condition or fully liquid undercoated condition.

With the co-deposition aspect of the present invention it is essential that the surface onto which the particles of the base material and the alloying or reactant addition are co-deposited is not at too low a temperature as this leads to individual particle of the base alloy retaining its own indentity. Conversely, the surface onto which the particles are co-deposited must not be at too high a temperature as a thick layer of molten alloy can build up on the surface of the deposit and subsequently be ejected from the surface by the high velocity gas and/or any motion of the collector.

Ideally, the conditions of co-deposition are controlled in such a manner that a layer of semi-solid/semi-liquid metal of controlled thickness is maintained at the surface of the deposit throughout the co-deposition, so that individual particles from the base alloy lose their identity in the semi-solid/semi-liquid layer. The atomised particles of the base material in which dendrite solidification has occurred during flight are impacted at high velocity onto the surface of the deposit resulting in dendrite fragmentation. The fine pre-solidified particles and the coarse fully molten particles of the base alloy add to the solid and liquid content of the surface of the deposit. Thus the deposit surface consists of a mixture of dendrite fragments of the base material particles, pre-solidified particles of the base material and liquid metal from the base materials together with the alloying or reactant addition. The fine pre-solidified particles of the base material, alloying or reactant addition and the dendrite fragments partially re-melt in the liquid metal, aided partly by the release of latent heat and the metal solidifies uniformly and rapidly as the atomising gas flows over the surface of the deposit. During this operation the alloy or reactant addition may then melt and/or diffuse into the base material to form a deposit of the desired integrated alloy, or alternatively, the material may chemically react with the matrix alloy or some constituent of the matrix alloy or of the gas or with a specially added constituent to the gas to reduce porosity in the deposit or to form a second stable phase.

Post heat treatment or hot working may be necessary in some cases to complete the diffusion or reaction processes.

As explained above the addition need not be applied by the introduction of separate particles which co-deposit into the base material. For example, the atomisation of copper with nitrogen as the atomising gas invariably results in 1 to 4% porosity in the deposit. This is because nitrogen is inert with respect to copper. By deliberately doping the copper base material with a trace of aluminium, which reacts with the nitrogen, the porosity in the end product may be reduced to less than 1%. Moreover, whilst aluminium nitride is normally detrimental to the properties of an ingot due to segregation the formation of large precipitates, the rapid solidification of a spray forming process means that the nitride is small and evenly dispersed and does not constitute a problem. The copper desposit so formed has a large grain size. If it is desired to reduce the grain as well, this can be achieved by the addition of small amounts of oxygen in the atomising gas (suitably by the inclusion of air) which will provide a deposit with a finer grain size and still with less than 1% porosity. The free grain size produced during spray deposition can be retained in the copper alloy if the grain boundaries are prevented from moving after solidification is completed. This is achieved by forming very fine oxide particles during atomisation that pin the boundaries and so produce a material at room temperature with a grain size of 15-25µ. Two similar melts can be combined to produce a base alloy having extra precipitate formed by reaction between two or more compounds of the two melts. For example, a high aluminium stainless steel melt may be mixed with a high oxygen stainless steel melt to produce an alloy containing a fine dispersion of alumina. In another example, two copper melts, one containing zirconium and one containing boron can be co-deposited so that an alloy with a fine dispersion of zirconium boride would be formed.

Another example is in a nitrogen atomised Nickel base alloy where pores as large as 100 microns might be present in the deposited material leaving a porosity of 3 to 5%. By adding to the nickel a reactive addition such as aluminium and titanium which can be combined with nitrogen trapped in the deposit, the pore sizes can be reduced to less than 5 micron and the overall porosity to less than 1%.

The reactive addition need only be present in very small quantities and yet have a significant beneficial effect on the final deposit. For example, in the case of the pure copper the addition of <0.25% aluminium will result in a significantly reduced porosity in the deposit formed by nitrogen atomisation.

The invention will now be described with reference to the following particular examples:

Example 1

This example relates to producing an alloy whose composition prevents successful atomisation because of nozzle blocking problems. Thus gas atomised powders cannot be produced for subsequent compaction into solid parts. In addition, spray deposits cannot be produced for the same reason. This is the case for stainless steels which contain high aluminium additions. However, the application of aluminium powder into the spray allows a much higher aluminium content to be achieved whilst avoiding blockage of the pouring nozzle. The aluminium powder co-deposited with the stainless steel base material melts in the deposit because of its lower melting point (660°C) and the aluminium diffuses very rapidly into the steel. In this way it is possible to produce a stainless steel/aluminium alloy having up to 20% aluminium. This can provide a material with increased corrosion resistance and improved metallurgical properties.

Example 2

In this example the base material is a titanium alloy which is atomised and to which is applied particles of silicon carbide of a fine particle size e.g. 10 micron. The titanium reacts with the silicon carbide causinng precipitation of fine titanium carbide in a titanium matrix.

Example 3

This examples relates to the application of an addition to the metal to reduce porosity in the final deposit and to the atomising gas to modify the structure of the deposit.

A copper, 0.5. wt% aluminium alloy was melted and poured from a crucible via a zirconia nozzle into the gas atomising chamber. High purity nitrogen gas was used to atomise the stream. The gas to metal ratio used was 0.63 cum/kg. At a distance of 430mm from the atomisation point a rotating ceramic disc was used to collect the spray and a solid deposit was built-up. After 5 seconds spraying time (20% of total spray) a small amount of air was added to the atomising gas which raised the chamber O_2 content from 20 ppm to 500ppm O_2. There was no noticeable effect on the spray.

On examination it is found that the first material sprayed had noticeably less porosity than pure copper atomised previously under the same conditions. It is believed that this is due to a reaction between the aluminium in the copper alloy and a small amount of nitrogen atomising gas which remains trapped.between droplets forming every fine precipitates of aluminium nitride. For the pure copper, in the absence of the aluminium addition, the nitrogen expands in the hot deposit to form gas porosity.

When the oxygen was added to the atomising gas the structure of the deposit was altered instantly. The grain size of the nitrogen atomised alloy was 200 microns whereas with some O_2 in the atomising gas the grain size was reduced to 20-30 micron. The mechanism for this is yet to be determined, but we believe that Al_2O_3 is formed in the spray and decorates the grain boundaries immediately after solidification is complete and inhibits grain boundary movement and therefore grain growth during subsequent cooling and a subsequent hot working processes if employed. Without oxygen in the atomising gas, no precipitates of aluminium oxide are formed on grain boundaries and the grains can grow during subsequent slow cooling.

Further addition of O_2 into the atomising gas did not effect the microstructure but may alter the mechanical properties by increasing the volume percent of oxide so producing some dispersion strengthening.

Example 4

The experiment of example 3 was repeated using a medium carbon steel (0.35% C) with 0.25% Al added. Normally this material is porous after spraying with nitrogen gas. At the start of the run the porosity was reduced significantly because of the aluminium, due the formation of aluminium nitride (AlN). However, when the oxygen was added the remaining porosity was almost totally eliminated. The reason for this is being further investigated as well as the effect of the resulting alumina and aluminium nitride precipitate on the mechanical properties of the alloy.

The experiments of examples 3 and 4 show that the addition of nitride formers to an alloy can alter the structure of the spray deposit. The compound formed may refine the grain size and/or alter the properties of the alloy.

Consequently, by deliberately adding reactants to the material to be atomised, or adding gaseous reactants to the atomising gas or by injecting particulate reactants, either in solid or molten form, and subsequently co-depositing it is possible to create new material compositions specifically designed for the spray deposition method of forming.

Claims

1. A method of spray deposition comprising the steps of:

teeming a stream of molten metal or metal alloy or non-metal base material through an atomising device,

directing atomising gas at temperature less than that of the liquidstream to break up the stream of the base material into a spray of atomised droplets, and

applying an addition or a reactant material which is deliberately added for at least one of reaction with the base material, reaction with the atomising gas, diffusion within the base material and evolution of a gaseous phase within the base material.

2. A method according to claim 1 wherein the applied addition or reactant msaterial is in the form of applied liquid or solid particles the method comprising the further steps of

directing the spray and applied particles at a collector so as to co-deposit thereon, and

controlling the operating conditions such that the composition of the base material of the deposit so formed is changed as a result of the presence of the applied particles.

3. A method according to claim 2 wherein the applied particles are selected from metal, metal alloy, non-metallic material, compounds or ceramic.

4. A method of producing an alloy by spray deposition comprising the steps of atomising a stream of molten metal or metal alloy base material to form a spray of atomised metal particles by subjecting the stream to atomising gas directed at the stream, and introducing into the spray of atomised or atomising particles of the base material, or into the molten stream just prior to atomising, solid or molten particles of a different metal, metal alloy, ceramic or a non-metallic material to form an alloying addition to the base material and co-depositing the particles of the base material and the alloying material under controlled conditions such that the deposit formed comprises an alloy of the base material and the alloying addition.

5. A method according to claim 4 wherein partial or complete alloying occurs on deposition or on subsequent cooling.

6. A method according to claim 4 wherein partial or complete alloying is carried out by diffusion during subsequent heat treatment or hot working.

7. A method of injecting into a spray of atomised particles of a base alloy, solid or molten particles of a metal alloy, ceramic or non-metallic compound which

during flight or subsequently on or after deposition, reacts with the base alloy to form a dispersoid composed of constituents from both the base alloy and the injected solid or molten particles.

8. A method according to any of claims 2 to 7 wherein particles are applied by generating a fluidised bed of the alloying particles and transporting the particles in a gas stream from the bed into the stream or spray so that the alloying addition particles are co-deposited with the atomised base material particles.

9. A method of spray deposition according to claim 1 wherein the reactive addition is applied to the atomising gas and/or the metal or metal alloy of the base material in order to reduce or eliminate porosity caused by gas entrapment in the forming deposit by initiating a reaction between the entrapped gas and a constituent of the reactive addition or between the entrapped gas and a constituent of the deposit which is a reaction product of the base material and reaction addition.

10. A method according to claim 9 wherein the reactive addition reduces, by reaction, the porosity in the forming deposit and provides dispersion strengthening of oxide or nitride particles formed by the reaction.

11. A method of spray deposition according to claim 1 wherein the reactive addition is applied to the atomising gas and/or the metal or metal alloy of the base material in order to produce a controlled level of porosity by reaction between constituents of the reactive addition and that base material or the atomising gas.

12. A method of forming a deposit from gas atomised metal or metal alloy comprising doping the metal or metal alloy and/or the atomising gas with a material which will react on deposition to reduce the porosity in the deposit which would otherwise have been present without the addition of said material.

13. A method according to claim 12 comprising deliberately adding reactive material to the alloy to form a constituent which would not normally be acceptable in conventional forming techniques due to segregation problems but which, in the rapid solidification of an atomising process, improves the density and/or the microstructure of the deposit.

14. A spray deposit formed by the method of any of claims 1 to 13.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 88/01106

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^4: C 23 C 4/12

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^4	C 23 C; B 22 D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

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A	FR, A, 2012909 (JOHNSON, MATTHEY & CO.) 27 March 1970, see claims 1-12 --	1,2,3,7, 10,14
A	DE, B, 1102522 (FELIX RITTER VON RÜLING) 10 March 1961, see claims 1-9; page 3, left-hand column, lines 17-36 --	1
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A	US, A, 3663206 (THE BRITISH IRON AND STEEL ASS.) 16 May 1972, see claims 1,10-14 --	1
A	FR, A, 1412272 (DELORO STELLITE) 16 August 1965, see claims --	4,5
A	GB, A, 1531222 (VANDERVELL PRODUCTS) 8 November 1978, see claim 1, page 1, left-hand column, lines 19-23, 31-34 --	4

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* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search 3rd April 1989	Date of Mailing of this International Search Report 27. 04. 89
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer P.C.G. VAN DER PUTTEN

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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A	Patent Abstracts of Japan, vol. 9, no. 91, (C-277)(1814) 19 April 1985 & JP, A, 59222566 (KAWASAKI JUKOGYO) 14 December 1984, see abstract --	6
A	US, A, 4066117 (IAN SIDNEY REX CLARK) 3 January 1978, see claims 1,14	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 8801106

SA 25980

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 18/04/89
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