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(54) Making composite metal deposit by spray casting.

(57) A laminated composite metal deposit is made by providing a first metal stream a second metal stream and a substrate, atomising the two streams to form first and second sprays of hot metal particles by subjecting the streams to relatively cold gas directed at the same stream and depositing the sprays alternately on the substrate. The two streams may be different alloys of the same base metal, e.g., aluminium, and either may contain fibres, whiskers or particles of refractory material.

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MAKING COMPOSITE METAL DEPOSIT BY SPRAY CASTING

This invention is concerned with a method of making a composite metal deposit by spray casting. The technique of spray casting is well known and comprises the steps of atomising a stream of molten metal to form a spray of hot metal particles by subjecting the stream to a relatively cold gas directed at the stream, and despositing the spray on a substrate. The provision of rapid and controlled cooling permits the production of deposits having unusual microstructures, which can be rolled or formed into shaped articles. But with only one source of molten metal, there is a limit to the range of compositions and microstructures that can be obtained.

GB 8606733 describes a spray casting method which includes the step of applying to the stream or spray fine, solid particles of a material of different composition from the metal. The particles are incorporated in the deposit. The use of refractory particles e.g. of alumina or silicon carbide can result in metal matrix composites having enhanced properties.

US Patent 4522784 describes a casting method in which two streams of molten metal are mixed just prior to casting, the smaller stream having a higher temperature than the larger stream and being chosen so that a fine intermetallic precipitate is formed during and prior to casting. With the DC casting methods described, it is difficult to remove heat fast enough from the system to prevent to re-solution of the intermetallic precipitates.

GB 1359486 describes a spray casting technique for casting two immiscible metals of different density. A single flow of molten metal consisting of concentric streams of the two metals is atomised and the drops collected on a substrate. The range of alloy compositions that can be cast in this way is quite restricted.

This invention provides a convenient way of making composite metal deposits by spray casting, which is characterized over the above prior art by the fact that separate streams of molten metal are atomised separately. As a result, there is much less restriction on the compositions of the two metals.

GB 1083003 describes a method of making bearing materials by spraying A1 and Pb simultaneously onto a backing strip. This results in a microstructure comprising alternating regions, of size corresponding (substantially) to the molten spray droplets, of A1 and Pb. US 3826301 contain a similar disclosure.

The invention provides a method of making a composite metal deposit which method comprises providing a first metal stream, a second metal stream and a substrate, atomising the two streams to form first and second sprays of hot metal particles by subjecting the streams to relatively cold gas directed at the streams, and depositing the sprays consecutively on the substrate to form thereon a laminated depost.

The first and second metal streams may be provided by gravity flow from holding vessels containing supplies of the molten metals. The invention contemplates the use of two, three or more molten metal streams, each being atomised separately, and references to first and second metal streams should be construed accordingly.

Atomisation conditions may be chosen, as is known in the art, to control the size, velocity, direction and temperature of the sprays of hot metal particles. On being atomised, the particles of molten metal spread out in a conical spray pattern, which may be of circular cross-section or may be modified, as known in the art, to form a different cross-section or a more even spread of metal particles.

The substrate may be a metal surface, which may for example be flat or tubular with the metal spray to be deposited on the inner or the outer surface. It is generally preferred that the metal particles be still at least partially liquid on impact, otherwise the deposit may be too porous. By suitable control of the atomising conditions, the metal spray can be arranged to be partially or fully liquid but super-cooled on impact, so that solidifcation takes place immediately on impact and there is no need to extract large amounts of heat through the substrate.

It is possible to provide fibres, whiskers or particles of refractory material, e.g. carbon or silicon carbide, on the substrate in such a way that they become embedded in the coherent composite metal deposit and provide reinforcement for it. Also if desired, particles of refractory material can be incorporated in the first and/or second spray by the technique described in GB 8606733 noted above.

Three (or more) sprays may be used. For example the spray patterns of two may be superimposed and operated simultaneously. This can result in a laminated structure in which alternate layers have a microstructure resulting from these two sprays. Or two superimposed sprays may be chosen to interact as described in the aforesaid US patent 4522784.

There is no critical range of ratios of the two metals constituting the first and second sprays. Suitable proportions of the two (or more) metals are chosen for particular applications. The spray patterns of the first and second sprays may, but need not, overlap; that is to say, the two sprays may be arranged to impact on the same or different areas of the substrate. The substrate may be translated, or reciprocated, or rotated in order to pick up the two metal sprays. These features can be used to exercise further control over the structure of the deposit. For example, if the spray patterns of the two sprays do not overlap and the substrate is reciprocated between them, the deposit may consist of alternating layers of first and second metal.

If the spray patterns of the two sprays do overlap, then it is necessary to operate the two sprays alternately in order to achieve the desired laminated structure. In order to operate both sprays continuously, it is therefoe preferred that the two spray patterns can be arranged not to overlap, and to reciprocate or rotate the substrate so that alternating layers of the two metals are deposited thereon.

Other variations in structure can be achieved by supplying one of the metal streams continuously and the other only intermittently. Or a first metal stream may be supplied initially, followed by the second, so that the deposit consists of the first metal with a surface coating of the second. The supply of molten metal in two or more streams gives the operator a great deal of latitude in determining the structure of a deposit.

Preferably, the laminated deposit comprises at least two layers of each metal in alternating superimposed relationship. The thickness of the alternating layers has a significant effect on the properties of the laminate. In the as-sprayed deposit, each layer preferably has a thickness in the range 0.01 - 100 mm, particularly 1 - 10 mm. The as-sprayed deposit may be subjected to rolling. For many purposes it is preferred that each layer in the rolled product have a thickness of from 10 to 500 microns, particularly 30 to 200 microns.

Since the two metals do not contact one another prior to deposition on the substrate, which may be followed by immediate solidification, there is very little restriction on the nature of the metals that may be used. It would be disadvantageous if the temperature of one metal on deposition were so high that substantial melting of the other took place on the deposit. It is often convenient to use two different alloys of the same base metal. The method is of particular interest for spray casting aluminium alloys, for which purpose an inert gas such as argon or nitrogen is generally desirable though not essential.

Reference is directed to Figures 1 to 3, each of which is a schematic diagram of a system for making a composite metal deposit according to the invention. Referring to Figure 1, the system comprises first and second furnaces 10 and 12 for supplying first and second streams of molten metal, which are atomised (by means not shown) to form first and second sprays, 14 and 16, of hot metal particles. The spray patterns overlap, and each spray is operated in turn while the other is shut off. The sprays are deposited in turn on a substrate 18, whose position and orientation are controlled by means 20. The metal sprays and the substrate are contained within a spray chamber 22, which is closed except for an exit vent for gas and any overspray powder.

A refractory material contained in a stream of carrier gas is supplied via a pipe 26 to the region where the first metal is atomised, and becomes incorporated in the first metal spray 14.

In the system shown in Figure 1, the substrate 18 might be maintained stationary, so as to build up a composite metal body thereon; or it might be translated, rotated or reciprocated in order to build up a uniform composite metal layer. the substrate 18 might have taken the shape of a mould, with the intention of working the deposit while on the substrate to form a shaped article. In the system shown, provided that the metal drops are still liquid on impact, the deposit will be substantially non-porous and will comprise alternating layers of the first and second metals.

Figure 2 corresponds to Figure 1, except that the spray patterns of the two metal sprays 14 and 16 are shown as being non-overlapping. In this case, the sprays are operated continuously and the substrate 18 is reciprocated in order to obtain a deposit consisting of alternating layers of first and second metal.

In Figure 3, the spray patterns of the two metal sprays 14 and 16 are shown as partly overlapping when they impact on cylindrical substrate 18 which is caused to rotate round a horizontal axis 28. A fibre 30 is supplied from a spool 32 and becomes incorporated in the deposit.

There follow examples of combinations of metals and alloys that can be used to make composite metal deposits according to this invention. In each case, the first metal or alloy mentioned will generally be present in the deposit in a volume concentration as great or greater than the second metal or alloy.

A. The first metal is the alloy designated 7010 in the Aluminum Association Register, and the second metal is a softer Al alloy such as 6061 or pure Al metal. 7010 is typically used for aircraft structures, and the second metal improves fracture toughness by a micro-laminated structure to reduce fatigue and blunt cracks.

B. The first metal is 7010 alloy and the second metal is 6010 alloy to confer ductility, toughness and fatigue resistance.

C. The first metal is 7010 alloy and the second metal is an Al/Zn alloy to improve stress corrosion resistance.

D. The first metal is 7075 alloy, used for armour plating, and the second metal is an Al/Si alloy to increase resistance to spalling.

E. The first metal is 7075 alloy, and the second metal is Pb to increase density, improve ballistic properties, and provide a microstructure to break up shock waves.

F. The first metal is any Al alloy and the second metal is Zn, applied on the surface as a layer amounting to 1 to 5% of the total thickness of the deposit, to aid diffusion bonding.

G. The first metal is 6061 alloy and the second metal is 7475 alloy + SiC to provide a product having improved ductility and toughness.

EXAMPLE

Laminated material was sprayed using a combination of 6061 Al alloy from on atomizer and 7475 Al alloy + SiC from the other atomizer.

1. Spraying conditions.

Both crucibles used were alumina with zirconia nozzles. the atomizing gas was nitrogen. The collector was an aluminium plate 300 mm long by 150 mm wide. The plate was reciprocated beneath the sprays at a frequency of 1Hz.

The following are the spraying conditions for the 6061 alloy

Temperature of melt		=	730°C
Primary gas	Pressure	=	1.8 bar
	Flow rate	=	0.6 m^3/min
	Velocity	=	240 m/sec
Secondary gas	Pressure	=	5.5 bar
	Flow rate	=	8.0 m^3/min
	Velocity	=	300 m/sec

The conditions for the 7475 alloy were the same apart from the melt temperature which was 710°C. SiC particulate (F600) was fed to the 7475 spray only, SiC was fed at a rate of 1.72 kg/min to the atomizing nozzle.

Several batches of material were made using similar conditions.

2. Microstructure of product

Measurements of the elemental distribution across the bands indicate that there has been a degree of interdiffusion between adjacent layers indicating that an effective metallurgical bond has been made between them. The SiC content of the 7475 layers was 10-12% by volume.

3. Mechanical properties

The as - sprayed material was consolidated by hot rolling at 430°C to approximately 2 mm in thickness and then further cold rolling to 1 mm. Any as - sprayed porosity was found to close up during this process to form a fully consolidated product. The sheet was solution heat treated by holding for at least 30 min at 500°C and cold water quenching. The material was artificially aged for 20 hr at 120°C.

Tensile properities were determined on several batches of sheet containing different thicknesses of laminate. The following table contains a summary of the results.

Material	0.2% PS (MPa)	TS (MPa)	Ef (%)
5 layer laminate (=200 micron layers)	270	369	4.4
17 layer laminate (=70 micron layers)	273	406	9.9
7475 alloy with SiC	525	581	1.7
6061 alloy	240	260	8.0
6061 alloy with SiC	322	340	0.9

Crack initiation and propagation were also determined with the following results.

Material	Initiation energy (J/m^2)	Propagation energy (J/m^2)
5 layer laminate (=200 micron layers)	13433	40597
17 layer laminate (=70 micron layers)	17623	55788
7475 alloy with SiC	3189	8182

These results illustrate that the combination of the two materials in the laminate can result in improvements in mechanical poperties over the individual constituents. In this instance the results indicate an improvement in strength and ductility over 6061 and an improvement in ductility and crack initiation and propagation energy (indicating improved toughness) over the 7475 alloy with SiC. The results also indicate a significant improvement in the properties (notably ductility) over that of the 6061 alloy with SiC. It is also notable that the thickness of the laminated regions is highly important in controlling the final properties of the material -specifically in this instance the ductility and toughness of the laminate.

Claims

1. A method of making a composite metal deposit which method comprises providing a first metal stream, a second metal stream and a substrate, atomising the two streams to form first and second sprays of hot metal particles by subjecting the streams to relatively cold gas directed at the streams, and depositing the sprays consecutively on the substrate to form thereon a laminated deposit.

2. A method as claimed in claim 1 wherein the atomising conditions are controlled such that the first and second metal sprays are still at least partially liquid on impact on the substrate.

3. A method as claimed in claim 1 or claim 2, wherein there are provided fibres, whiskers or particles of refractory material on the substrate in such a way that they become embedded in the coherent composite metal desposit.

4. A method as claimed in any one of claims 1 to 3, wherein particles of a refractory material are applied to the first or second metal or spray.

5. A method as claimed in any one of claims 1 to 4, wherein the spray patterns of the first and second sprays do not overlap.

6. A method as claimed in any one of claims 1 to 5, wherein the first and second metals are different alloys of the same base metal.

7. A method as claimed in claim 6, wherein the base metal is aluminium.

8. A method as claimed in any one of claims 1 to 7, wherein the laminated deposit comprises at least two layers of each metal in alternating superimposed relationship.

9. A method as claimed in claim 8, wherein after rolling the deposit each layer is from 10 to 500 microns thick.

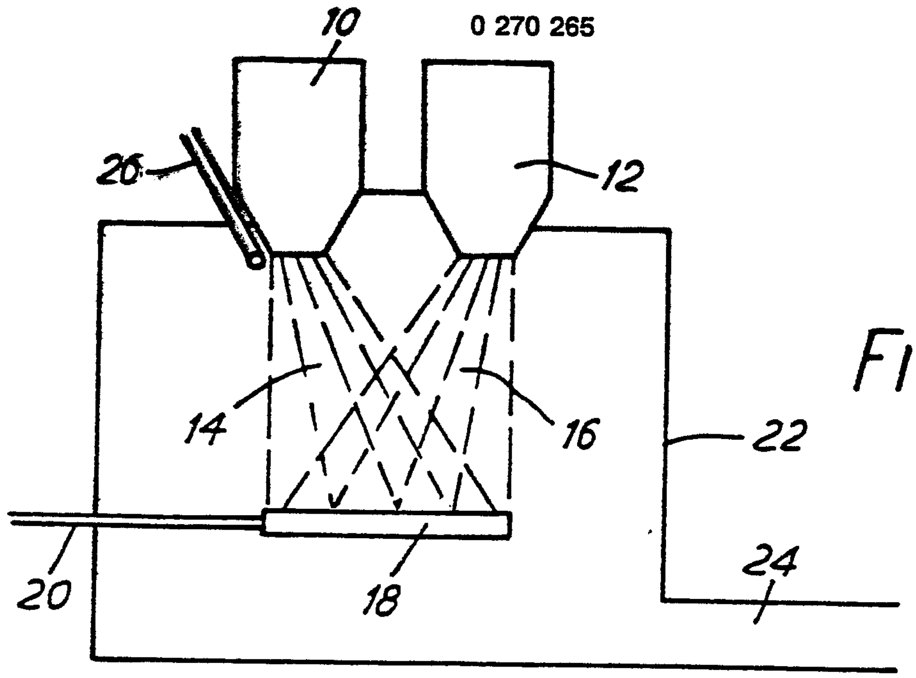

FIG. 1

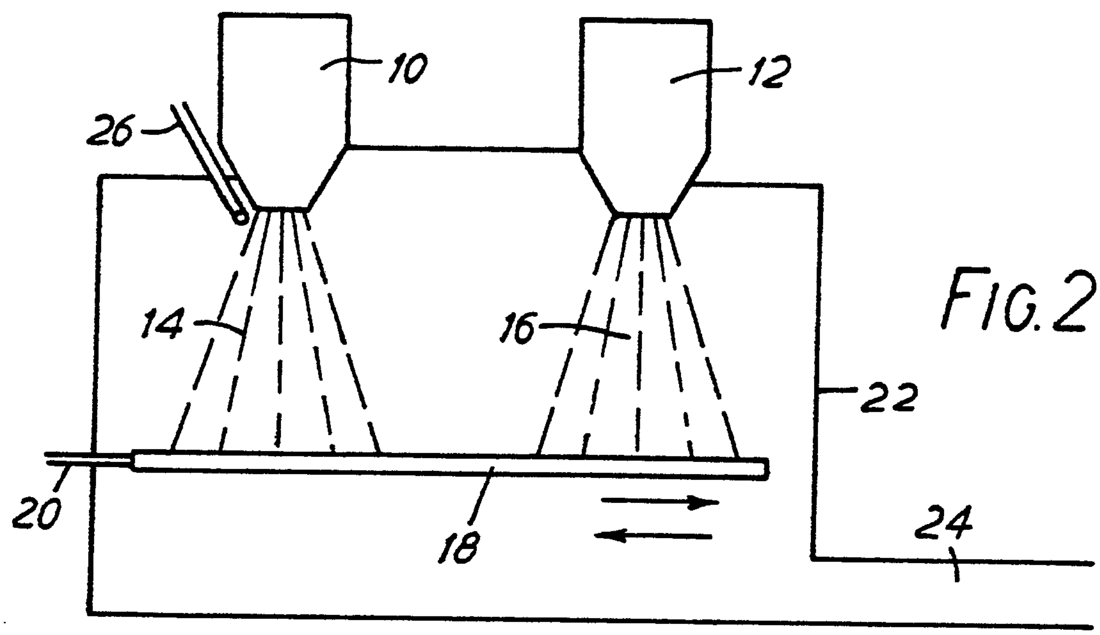

FIG. 2

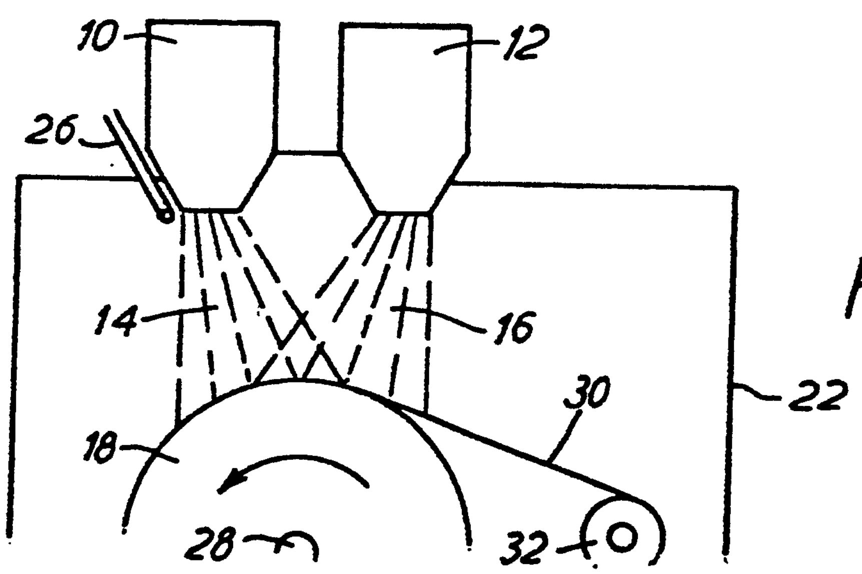

FIG. 3

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EUROPEAN SEARCH REPORT

Application Number

EP 87 30 9972

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X,D	US-A-3 826 301 (REGINALD GWYN BROOKS) * Figure 1; claims 1,3,4,5,6,7,11; column 4, lines 59-68; column 2, line 45; column 3, lines 54-61 *	1,2,4,5,6,7,8	C 23 C 4/12 C 22 C 1/10
A,D	GB-A-1 083 003 (THE GLACIER METAL COMPANY) * Figures 1-3; page 3, lines 91-104; claims 1,6,9,10,13,19; page 2, lines 15-21 *	1,2,6,7	
A	GB-A-1 410 169 (JOHNSON, MATTEY) * Figure 1; claims 1-27 *	1,8	
A	GB-A-1 531 222 (VANDERVELL PRODUCTS) * Claim 1; page 1, lines 9-30 *	1	
A	DE-A-2 439 620 (MEBAC) * Figures 1-4; claims 10-15 *	3	
A	FR-A-2 156 889 (BRITISH STEEL CORPORATION) * Claims 1-3 *	5,7	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	FR-A-2 311 101 (KAWASAKI JUKOGYO K.K.) * Claims 1-7 *	8	C 23 C B 22 F B 22 D F 16 C C 22 C
A	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 268 (C-197)[1413], 30th November 1983; & JP-A-58 147 556 (HITACHI SEISAKUSHO K.K.) 02.09.1983 * Abstract *	7,8	
A	US-A-2 993 264 (H.E. GRENOBLE) * Figure 7; claims 1-4 *	8,9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	05-02-1988	ELSEN D.B.A.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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