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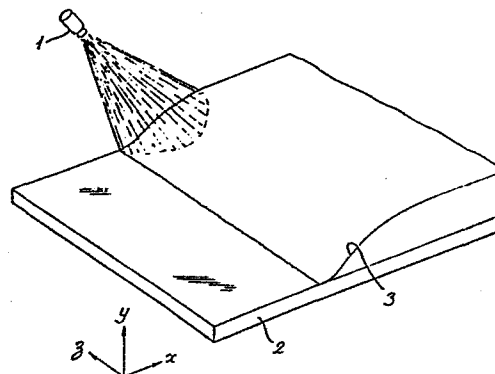
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64 **Spray deposition of metal.**

57 A process of producing a metal body comprises atomising a source of molten metal and directing the atomised molten metal particles, as a spray, onto a cooler substrate, on which the molten metal particles splat and build up to form a deposit, characterised by controlling the spray conditions so that the whole, or most, of the surface of the deposit is molten throughout the process.

The control may be in response to visual monitoring of the surface, and may also ensure that the molten layer does not become so thick that bulk lateral flow becomes possible. Thereby, segregation-free 'incremental solidification' is possible. The product is typically strip or sheet.



SPRAY DEPOSITION OF METAL

This invention relates to a process of producing a metal body by depositing sprayed particles. British Patent Specification 1262471 describes a way in which strip and sheet can be produced by directing a stream of molten gas-atomised metal particles on to a moving substrate to form a deposit which is subsequently hot worked to form the required product. A more recent research investigation (Metals Technology, February 1983, pages 61-68) has revealed and analysed various mechanisms that can operate during the spray deposition process itself, thereby giving rise to differing structures in the deposit.

It has now been found that failure to select appropriate conditions for spray deposition for each melt or alloy may lead to poor mechanical properties even after enough hot working to ensure full densification. In such cases, further hot deformation (which is liable to cause anisotropy), and possibly intermediate annealing or sintering, may be needed to achieve otherwise good mechanical properties. These additional treatments may render the process uneconomic and unattractive. It is therefore important to arrange matters such that the conditions of spray deposition are correct, as follows.

With low spray density coupled with high rates of cooling, as explained in the Metals Technology paper, the average molten droplet of a spray lands on the preceding splat after that splat has fully solidified; thus a layered deposit is build up, each layer consisting of a splat thickness. If the spray density is higher or the rate of cooling is lower, the average molten droplet of a spray lands on the preceding splat before the top surface of that splat has solidified; thus the two liquids mix, and the deposit hence shows little evidence of layering.

Small amounts of oxygen derived from the air may have a disproportionate effect on the behaviour of the deposits during subsequent hot working, and on the mechanical properties of the product. Air is difficult and expensive to exclude completely

from industrial operations. Protective atmospheres rich in CO or H_2 will counteract the effects of oxygen on iron and many steels such as carbon steels but not on metals and alloys such as Al, Ti and chromium-steels, which have a very high affinity for oxygen. There, formation of the metallic oxides is practically inevitable and one has to minimise the harm they do.

If for example a deposit of Al is made at low spray density and with a high rate of substrate cooling where merely normal industrial precautions are taken to exclude air, each droplet of spray typically becomes coated with a very thin, say 10^{-8} m, skin of Al_2O_3 , which is very strong, insoluble, tenacious yet brittle, and cannot be reduced by any gas at reasonable temperatures. In addition the preceding (solidified) splat is also covered with a similar oxide skin.

As it lands, each molten droplet breaks its oxide skin, revealing new unoxidised metal instantaneously. The surface area of the new splat (formed from the droplet) is typically 2 to 20 times as large as was the surface area of the droplet. Its brittle oxide skin is fragmented and only plays a minor part in subsequent events. The oxide skin on the fully solidified preceding splat stays intact however, and forms a continuous boundary between the new splat and the preceding splat. The subsequent deposit structure is layered, lacks coherence and has poor mechanical properties because of the presence of the intervening oxide film.

When the deposit is subsequently hot worked the brittle oxide skins are gradually broken up, but strains of say 60%-90% or long times of high temperature sintering are necessary to give good mechanical properties; such treatments are costly and may be undesirable technically.

Contamination with oxygen being industrially unavoidable as already mentioned, operating conditions must be selected so that its most deleterious effect - a thin unbroken skin of oxide as just described - is avoided. This can be accomplished for example by using a higher spray density or a lower rate of cooling, so that, in consequence, each average droplet now lands on the

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preceding splat before the top surface of that splat has fully solidified. Both the droplet and the molten top surface of the splat are covered with a very thin skin of oxide but, when the two liquid surfaces meet, the consequent turbulence breaks both these skins and disperses the fragments. The two liquids mix and on subsequent solidification give a non-layered structure that has coherence and reasonable ductility because the very small fragments of oxide are no longer present as continuous skins or films but as dispersed discontinuous fragments.

These measures are useful not only for aluminium, but also for such elements as Mn, Mo and W (even though their oxide skins are more easily dispersed and hence rendered relatively innocuous), and also for iron or carbon steel (where otherwise a reducing atmosphere rather than an inert atmosphere might be necessary), and can be used for any other metal, even such as copper. In this connection, the solid solubility of an oxide in its own molten metal has an effect. When this solubility is reasonably high, dispersed oxide films are more easily "balled-up" because of surface tension effects, Ti being outstanding in this respect (although large quantities of its oxide are still harmful). Iron oxides have a limited solid solubility in Fe but sufficient to enable any oxide films to re-aggregate as discontinuous particles and so become relatively innocuous.

According to the present invention, a process of producing a metal body (e.g. strip or sheet) comprises atomising a source of molten metal and directing the atomised molten metal particles (as a spray) on to a cooler substrate, on which the molten metal particles splat and build up to form a deposit, the deposit being optionally subsequently removed from the substrate, and optionally hot worked, the process being characterised by (for example by responding to monitoring the appearance of the surface of the deposit, or by programming) controlling the spray conditions, so that the whole, or most, of the surface of the deposit is molten throughout the process.

The purpose is to make certain that on average each molten particle lands on the preceding splat in that position while at least the top surface of that splat is still molten.

Preferably, the spray is directed so as to scan the directed
05 stream over a desired area of the substrate such that, at every point in that area, incremental casting conditions are maintained, i.e. the average droplet lands on the preceding droplet on the substrate while at least the top surface of that preceding droplet is still molten but the thickness of molten metal does not increase
10 beyond what is restrainable by the surface tension and viscosity of the molten metal. The programme to achieve this will maintain an arrival rate of metal droplets at any point commensurate with the rate of heat extraction from that point, thus allowing less metal to arrive at an already thickly coated place (where heat
15 will be lost slowly) and allowing more metal to arrive at a so far uncoated place (where heat will be lost quickly).

The programme may arise from closed-loop or heuristic feedback and may direct the control means to alter the conditions in various ways, for example, on the next cycle to
20 reach that point, to alter the scanning speed or the advance per line of scan.

Preferably the stream of droplets strikes the substrate at an angle.

Preferably the programme maintains the deposit at a thickness
25 which at any given point is substantially proportional to the square root of the distance of that point from the leading edge of the deposit.

The invention also provides a process for depositing a metal on a substrate by forming a source of molten metal into a directed
30 stream of droplets and controlling the direction of the stream according to a programme as set forth above.

It will be appreciated that the deposition of molten particles from a spray is a random process in which the precise behaviour of each individual molten particle cannot be known or predicted,
35 although the behaviour of the average particle can be clearly

defined. Thus, even with the most careful control, a small proportion of the molten particles will, by chance, land on a splat which has already fully solidified. Moreover atomisation itself is a random process, in which a small proportion (by weight) of the particles in a nominally molten spray will be solid by the time they land on a prior splat. This specification necessarily refers to the behaviour of the particles or splats as a whole, i.e. the behaviour of the average particle or splat.

To keep the surface of the deposit still molten, as required, at the instant that a new droplet lands on it, one or more of the spray conditions must be controlled, such as (mainly) speed and cooling rate of substrate, atomising gas flow, pressure and temperature, molten metal feed rate, spray scanning rate and temperature. Of these, the cooling rate of the substrate, temperature of atomising gas and molten metal temperature, while adjustable, cannot readily be used to correct and control short-term fluctuations in the process. Moreover atomising gas flow and pressure are usually linked by virtue of fixed nozzle dimensions. The spray conditions controlled by the process according to the invention are thus preferably the substrate speed, scanning rate, metal flow rate and gas pressure, the other conditions normally being fixed during any one run. Increasing substrate speed, increasing gas pressure and decreasing metal flow rate bring about more rapid freezing and decrease the depth of liquid on the surface of the deposit, and vice versa.

In one preferred mode of controlling the spray conditions, the appearance of the surface of the deposit is monitored (to check its molten-ness) and the spray conditions are controlled in response. The monitoring of the surface of the deposit may be by direct observation of the surface where deposition is occurring, and can be conducted visually, directly or through tinted or smoked glass. The observation may be by video, in which case there is advantage in having a picture "freeze" for a sequence of periods of, say, 1 second at a time. The observation can be by radiation pyrometry, or by reflectivity measurements (at preset angles) of the surface.

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If visual observation or video is used it will be clearly apparent when most of the prior splat surface is molten. By this is meant generally more than 80% and always more than 50%. The extent of the molten surface is shown by the fact that the molten
05 splat surface is smooth and bright, though rippled due to impinging gases and vibrations, compared with the solidified splat surface that is matt and immobile. With the unaided eye events happen so rapidly that only a general effect will be seen but this is quite distinctive. By "freezing" for short intervals using video the
10 picture becomes clearer and a more accurate assessment can be made of the situation.

Although because of the random nature of spray deposition some areas of the surface for a brief period will always solidify, it is preferable for the whole splatted surface to be molten
15 during deposition. However, the molten splat layer should not be allowed to become too thick, otherwise conditions will revert to those of conventional casting and some benefits of spray forming will be lost such as small grain size and avoidance of segregation. The fully molten layer should typically not be as thick as 1 mm,
20 but the precise thickness which should preferably not be exceeded depends in each case on viscosity and surface tension. We can recognise whether the thickness is excessive by seeing if massive ripples, or flow involving areas far larger than one splat, occur as a result of the gases impinging on the surface or, if the
25 substrate is being sprayed in an attitude other than horizontal, by seeing if the molten deposited metal runs off under gravity. Preferably, the monitoring of the appearance of the surface can recognise an excessively thick molten layer and can control the spray conditions accordingly.

30 Under typical control, the speed of the substrate, the pressure of atomising gas and the rate of flow of liquid metal from the nozzle are altered until a molten layer covers most or all of the depositing surface. Preferably these parameters are controlled additionally such that the molten layer is not too
35 thick.

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Radiation pyrometry can be used for the monitoring. In this case, after due allowance has been made for emissivity and absorption, the monitored temperature of the surface will indicate the average depth of liquid. If the average temperature of the deposited surface is at or below the solidus the average depth of liquid is too small. If the average temperature of the deposited surface is above the liquidus, the average depth of liquid is likely to be too great. In the case of a pure metal, the temperature of the surface must remain as close as practicable to the melting point. The spray conditions are controlled accordingly.

To produce strip or sheet, the spray may be scanned, that is, typically reciprocated over the width of the strip (transverse to the length, and direction of motion, of the strip). The scanning should be fast enough that the spray returns to any particular position before the top of the average preceding splat at that position has solidified, i.e. generally not less than 10 traverses per second. Otherwise, the resulting structure will be layered with bands of spray cast (molten preceding splat surface) interleaved with bands of spray deposited metal (solidified preceding splat surface), which is undesirable as it leads to heterogeneity. With fast enough scanning, visual observation or radiation pyrometry will be effective monitors and enable the necessary control of the process. Scanning, however, is amenable to an alternative mode of control, viz. programming to ensure incremental casting at any given point, as already mentioned.

In industrial-scale operation of the process, the deposit is always completely solid (i.e. temperature below the solidus) very soon after leaving the deposition area. This allows the product to be hot rolled "in line" without any danger of "hot tearing" or "hot shortness" as would be caused by plastic deformation if the deposit were above the solidus.

The invention will be described by way of example with reference to the accompanying drawing, which illustrates a slab being spray-deposited, with certain features greatly enlarged for clarity.

A spray head 1 produces a narrow cone of molten metal spray directed towards a cooled substrate 2, on which the resulting coating of metal may be hot-rolled or from which it may be stripped. The spray head 1 is to deposit a thick slab of metal, say 5 cm thick. The spray head moves back and forth parallel to the z-axis. The substrate lies in the x-y plane, and is withdrawn relatively slowly in the x direction. The spray is directed in the x-y plane, at 45° to the x-direction.

It can be shown that the profile 3 of the edge of the deposited layer should theoretically approach as closely as possible the form of a parabola. This would be impossible if the spray were applied in purely the y-direction and therefore, instead, it is applied with a substantial x-component, although, as indicated in the drawing, the actual profile deviates from a parabola.

The parabola shape can be seen to be intuitively reasonable since, at the very leading edge, molten droplets will directly strike the substrate - the coolest surface of all - and will freeze faster than 'incremental solidification' unless a fair thickness is applied quickly, whereas nearer the top of the deposition hill, heat extraction is slower and only a smaller thickness can be applied before exceeding the molten thickness tolerable as 'incremental solidification'.

The deposition zone can be extended for thicker deposits so long as some approximation to the square root law (i.e. parabola shape) is programmed, but eventually the deposition rate would become unpractically low. However gas convection and radiation heat transfer extends the practical upper limit of thickness of deposit. In the case of low-melting metals, heat loss by radiation is not important but gas convection becomes dominant at greater thicknesses.

In practice, incremental solidification conditions can be maintained through a substantial proportion of the thickness deposited, even though the deposition rate departs significantly from the ideal, demonstrating that there is a useful tolerance on the flow rate profile and on the thickness of the liquid layer.

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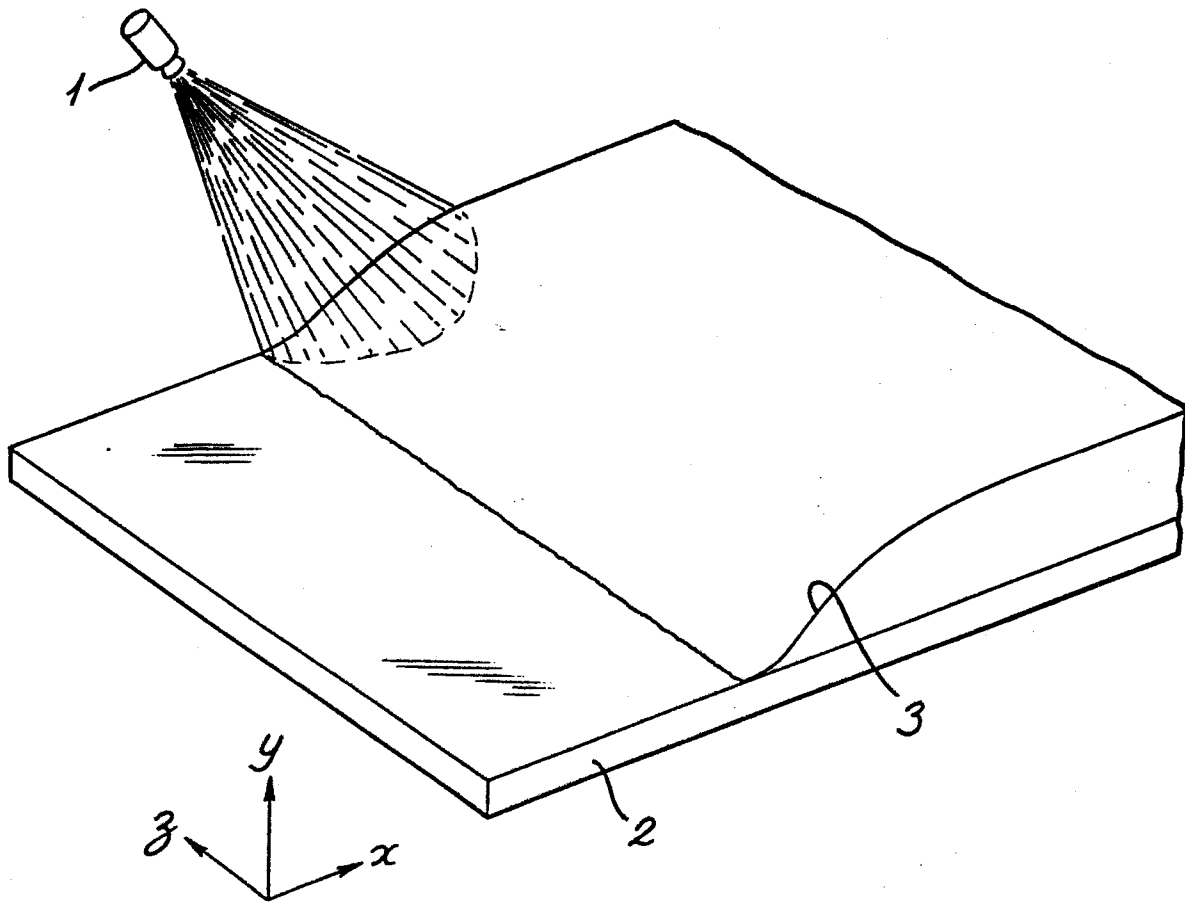
Control can be applied by varying the distance between the spray head 1 and the substrate 2. The solid angle of the spray from the spray head 1 could also be varied. The thickness applied in any one pass can also be controlled by the speed of scanning
05 and by the speed of advance of the substrate 1.

CLAIMS

1. A process of producing a metal body, comprising atomising a source of molten metal and directing the atomised molten metal particles, as a spray, onto a cooler substrate, on which the molten metal particles splat and build up to form a deposit,
05 characterised by controlling the spray conditions so that the whole, or most, of the surface of the deposit is molten throughout the process.
2. A process according to Claim 1, wherein the metal body produced is strip sheet.
- 10 3. A process according to Claim 1 or 2, wherein deposit is subsequently removed from the substrate.
4. A process according to any preceding claim, wherein the deposit is hot worked.
5. A process according to any preceding claim, wherein the spray
15 conditions are controlled by a programme which scans the directed stream over a desired area of the substrate such that, at every point in that area, the average droplet lands on the preceding droplet on the substrate while at least the top surface of that droplet is still molten but the thickness of molten metal does not
20 increase beyond what is restrainable by the surface tension and viscosity of the molten metal.
6. A process according to Claim 5, wherein the programme maintains the deposit at a thickness which at a given point is approximately proportional to the square root of the distance of
25 that point from the leading edge of the deposit.
7. A process according to Claim 5 or 6, wherein the stream of droplets strikes the substrate at an angle measured in a plane which does not include the leading edge of the deposit.
8. A process according to any of Claims 1 to 4, wherein the
30 appearance of the surface of the deposit is monitored, and the spray conditions are controlled in response to the monitoring so that the whole, or most, of the surface of the deposit is molten throughout the process.
9. A process according to Claim 8, wherein the directed stream
35 is scanned over a desired area of the substrate such that, at

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every point in that area, the average droplet lands on the preceding droplet on the substrate while at least the top surface of that droplet is still molten but the thickness of molten metal does not increase beyond what is restrainable by the surface
05 tension and viscosity of the molten metal.





DOCUMENTS CONSIDERED TO BE RELEVANT			EP 85300138.6
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, A	<u>GB - A - 1 262 471</u> (NATIONAL RE-SEARCH) * Claims *	1, 2	C 23 C 4/12 B 05 D 1/08

A	<u>GB - A - 2 115 014</u> (NATIONAL RE-SEARCH) * Fig. 1; claims *	1, 2	

A	<u>US - A - 3 995 073</u> (KUONEN et al.) * Fig; claims *	1, 4	

A	<u>DE - A1 - 2 823 817</u> (THE SECRETARY OF STATE FOR DEFENCE) * Fig; claims *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
A	<u>DE - A1 - 2 655 730</u> (GENERAL ELECTRIC) * Claims *	1, 4	C 23 C B 05 D

A	<u>DD - A - 87 453</u> (PURSCHE) * Column 2, lines 3-19 *	1, 4	

The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 03-04-1985	Examiner SCHÜTZ
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	