(CONVENTION. By one or more persons and/or a Company.) Form 4

600030

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

LODGED AT SUB-OFFICE
23 SEP 1987
Melbourne

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address (es).

~~We~~ / ~~I~~ (1) ALCAN INTERNATIONAL LIMITED,
of 1188 Sherbrooke Street West, Montreal, Quebec,
Canada

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)
PARTICULATE METAL COMPOSITES

(3) Here insert number(s) of basic application(s)

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered (3)
8622949

(4) Here insert Name of basic Country or Countries, and basic date or dates

for a patent or similar protection made in (4) United Kingdom
on 24th September 1986

~~APPLICATION AMENDED AND AMENDMENTS~~
~~FILED~~ 30-5-90

~~My~~ / Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys, 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 23rd day of September 1987

PATENT OFFICE ONE HUNDRED DOLLARS 100 PATENT OFFICE SIXTY DOLLARS 60

ALCAN INTERNATIONAL LIMITED
by
Stephen K. Plymin
Registered Patent Attorney

To:
THE COMMISSIONER OF PATENTS.

FEE STAMP TO VALUE OF $160 ATTACHED
MAIL OFFICER

(CONVENTION. Company) Form 8

COMMONWEALTH OF AUSTRALIA
Patents Act 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the Convention application made by Alcan International Limited (hereinafter referred to as the applicant) for a Patent for an invention entitled: Particulate Metal Composites

I, Dr. David Goodchild

of 77, Courtington Lane
Bloxham Oxon UK
OX15 4HS

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in Great Britain on the 24th day of September 1986, by Alcan International Limited.

3. RICHARD MICHAEL JORDAN - British of The Haven, Brewery Lane, Hook Norton, Oxon OX 15 5NX, England; IAN ROBERT HUGHES - British of 4 Sandell Close, Banbury, Oxon OX16 9LP, England and TREVE COURTNEY WILLIS - British of Flat 18 Britannia Heights, 34a Britannia Road, Banbury Oxon, England are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of the invention by virtue of an assignment dated 3 December, 1986.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at.....Banbury.....Oxon.....UK.....

this.....14th.....day of.....March.....1990....

.....

D. Goodchild

TO: THE COMMISSIONER OF PATENTS

(12) PATENT ABRIDGMENT (11) Document No. AU-B-78868/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 600030

(54) Title
AL BASE ALLOY - SIC PARTICULATE COMPOSITES

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(56) Prior Art Documents
US 4594101
GB 2146662
GB 2115014

(57) Claim

1. A particulate composite, made by combining molten metal droplets with fine refractory material, in which the particles have a continuous phase of the metal and a disperse phase, incorporated in the continuous phase, of the refractory material.

10. A method of making the particulate composite claimed in any one of claims 1 to 9, which method comprises atomising a stream of a molten metal to form a spray of metal particles by subjecting the stream to relatively cold inert gas directed at the stream, applying to the stream or spray fine solid particles of a refractory material, allowing the metal particles to solidify, and collecting the resulting particulate composite.

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Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

Name of Applicant : ALCAN INTERNATIONAL LILMITED

Address of Applicant : 1188 Sherbrooke Street West, Montreal, Quebec, Canada

Actual Inventor: RICHARD MICHAEL JORDAN, IAN ROBERT HUGHES and TREVE COURTNEY WILLIS

Address for Service : EDWD. WATERS & SONS,
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

PARTICULATE METAL COMPOSITES

The following statement is a full description of this invention, including the best method of performing it known to :- us

PARTICULATE METAL COMPOSITES

This invention relates to particulate composites in which the particles have a continuous phase of a metal eg an Al alloy.

EPA 105595 describes Al alloys containing substantial proportions of Cr, Zr and Mn. Rapid cooling of the molten alloy e.g. by spraying or splat-casting, results in a particulate solid in which the bulk of the alloying additions are retained in solid solution. This material can be consolidated by powder metallurgy techniques to a product which can be age-hardened at a temperature of 300° to 500°C and which retains its strength for long periods at temperatures of 150°C to 450°C.

EPA 128260 describes a technique employing metal vapour to make composite particles below 10 microns.

GB 2115014 describes a method of making a massive (i.e. not particulate) product by combining molten metal droplets with fine refractory material.

DE 2124199 describes an atomisation method of making metal powders whose particle surfaces are coated with fine refractory material.

EPA 147769 describes a method of making particulate composites of Al alloys with fine refractory material, by mechanical alloying.

GB 1548616 is one of a family of patents relating to the manufacture of spray deposited preforms from which articles of precise shape can be produced e.g. by forging, pressing or machining. A stream of molten metal alloy is atomised by means of high velocity jets of gas and the resultant spray of hot metal particles is directed onto a shaped collecting surface to form a coherent deposit. The patent describes how a proportion of the particles may miss the target and collect as a powder or aggregate of overspray material which is not convenient for re-cycling and, it is

implied, not useful for other purposes.

EPA 198607 describes a method of making a metal matrix composite comprising the steps of atomising a stream of molten metal to form a spray of hot metal particles by subjecting the stream to relatively cold gas directed at the stream, applying to the stream or spray fine solid particles of a material of different composition from the metal, and depositing the metal, having said fine particles incorporated therein, in coherent form on a collecting surface. The fine particulate material enhances physical and mechanical properties of the metal matrix. The metal may be Al and the particulate material may be SiC.

When the method of EPA 198607 is operated, a proportion of the metal particles is generally not deposited on the collecting surface, and is collected downstream as a powder or aggregate. The present invention is based on the following observation regarding the overspray. When a finely divided refractory material has been applied to the stream or spray of molten metal, the refractory material is found, not only in the coherent deposit formed on the collecting surface, but also associated with the metal in the overspray. The refractory material is present in the overspray, not only on the surface of the solidified particles of metal, but also rather uniformly distributed within the interior of the particles. This observation was unexpected. It had not previously been realized that the refractory material became associated with the molten metal spray prior to deposition on a collecting surface. Indeed, the prior art noted above indicates that such association would not take place.

The present invention provides a particulate composite, made by combining molten metal droplets with fine refractory material, in which the particles have a

continuous phase of the metal and a disperse phase, incorporated in the continuous phase, of the refractory material.

The invention is of particular interest when the metal is an Al alloy, as the technique of atomising molten Al alloys is quite well developed. But the invention is applicable to other materials that can be sprayed in the form of molten droplets, such as for example, steel, nickel, cobalt, copper, titanium and magnesium.

The particulate composite has been made by combining molten metal droplets with fine refractory material. Even when spray casting is carried out in an inert atmosphere, so far as Al alloys are concerned, the resulting particles necessarily have at least a thin oxide coating on their surface. The particles do not normally contain any internal oxide inclusions unless this is deliberately added in (or as) the fine refractory material. By contrast, a particulate composite of an Al alloy made by mechanical alloying would necessarily contain internal oxide inclusions.

The particles of the composite generally have a size in the range from 10 to 500 microns, preferably with an average diameter of from 20 to 80 microns. When the particles are formed by spray casting, their diameter can be controlled by controlling the atomising conditions, as is known in the art. Although they may be flattened, e.g. as a result of splat-casting, the composite particles are preferably spherical.

The refractory material may be another metal of higher melting point than the metal, but is preferably an oxide, boride, carbide or nitride. Ceramic materials of this kind, some of which are known as refractory hard metals, are well known, and preferred examples include SiC, Al_2O_3, MgO, TiC and boron carbide. These refractory materials are

preferably used in the form of particles having average diameters, below 50 microns and down to sub-micron size. Particles of 5 to 20 microns are often convenient to use.

In the composite particles, the disperse phase and the continuous phase are preferably present in volume concentrations of 0.5 to 50% and 99.5 to 50% respectively. Particularly when used in a volume concentration of 10 to 30%, high strength high modulus refractory powders can impart substantial strengthening and modulus properties to the composite.

The matrix metal may be an Al alloy containing on or more conventional age- and solution-hardening ingredients such as Zn, Mg, An, Si, Li, and optionally also one or more transition metal elements for grain refining purposes.

Or the Al alloy may contain at least one transition metal alloying ingredient having age-hardening, or solution strengthening properties, such as for example Cr, Zr, Mn, Fe, Co and Ce. Preferred are alloys containing 0.5% to 7% by weight Cr, 0.5% to 2.5% by weight Zr and 0.1% to 4.0% by weight Mn. These alloying ingredients are difficult to get into solid solution in Al by conventional means, but this problem is solved by the spray-casting technique described below. These transition metal alloying elements have the advantage of providing age-hardening properties at elevated temperatures typically in the range $300^{o}C$-$500^{o}C$.

The transition metal alloying ingredients are preferably present at least partly, and preferably totally, in solid (supersaturated) solution in the metal. When not in solid solution, the alloying ingredients should be present as a fine dispersion. To achieve this, it is necessary to cool the molten metal rapidly at about $10^{o}C$ sec for a fine dispersion,

and at about 10^{o}C sec for solid solution. Depending on particle size, these are cooling rates which can be achieved by spray-casting.

In another aspect, the invention provides a method of making the particulate composite herein described, which method comprises atomising a stream of the molten metal to form a spray of metal particles by subjecting the stream to relatively cold inert gas directed at the stream, applying to the stream or spray fine solid particles of a refractory material, allowing the metal particles to solidify, and collecting the resulting particulate composite.

Preferably, the solid particles of refractory material are applied to the stream of molten metal just before this is broken up into spray. In order to obtain spherical particles it is, of course, necessary that the metal particles solidify before impact with any solid surface. For Al alloys the inert gas may conveniently be argon or preferably nitrogen. Providing the oxygen partial pressure is sufficiently low, the composite particles come out spherical with no more than a thin coating of aluminium oxide. The spray of molten metal particles may be directed at a collecting surface, in which case a particulate composite is recovered as a by-product. Alternatively, the spray conditions may be chosen such that the metal particles solidify before impact with any solid surface.

The nature of the Al alloy is not critical to the invention. The method has been employed to make particulate composites using SiC as the refractory material with the following: commercially pure aluminium, AA 2014, 2024, 2618, 6061, 7075, 7475, 8090, LM 13, A 3210, Al-12% Si, Al-20% Si and Al-6% Sn.

The particulate composite is amenable to further processing via known powder metallurgy routes

such as canning, degassing, compacting and extruding to solid eg semi-fabricated or fully fabricated products. Possible applications include extruding directly to form air-frame structures; extruding bar and forging to give gas-turbine compressor blades or pistons for internal combustion engines; or extruding plate and rolling to sheet for the skins of aircraft.

Reference is directed to accompanying drawing which is a diagram of an atomisation system suitable for making particulate composites of the invention. The system comprises a molten metal nozzle 10 from which is passing by gravity a stream 12 of molten metal. Surrounding the molten metal nozzle is a primary gas nozzle 14, with apertures to direct a primary support gas flow 16, parallel to and surrounding the metal stream, to shroud and contain the molten metal. Surrounding the primary gas nozzle is a secondary gas nozzle 18 provided with jets 19 which direct a secondary atomising gas stream 20 towards the molten metal stream. The secondary gas stream contacts the molten metal stream a distance h downstream of the molten metal nozzle and atomises it into a spray 22 of metal particles.

The secondary atomising gas flow 20 defines a cone of height h and radius equal to the distance of the jets 19 from the metal stream 12. The refractory material 24, entrained in a carrier gas, is introduced into this cone via a pipe 26. The carrier gas flow rate is typically several orders of magnitude less than the flow rate of the secondary atomising gas 20.

The position at which the carrier material is introduced within the cone is not critical; it could for example be inside, rather than outside, the primary gas nozzle 14. If the distance h is sufficiently small, it is possible to dispense with the primary gas nozzle altogether.

The refractory material loading in the carrier gas, and the carrier gas flow rate relative to the metal flow rate and the secondary (atomising) gas flow rate determine the concentrations of refractory material in the particulate composite produced. The temperature and flow rate of the atomising gas determine the rate at which the atomised metal particles solidify.

The following examples illustrate the invention.

Example 1

A typical experiment resulting in the formation of composite powder (18% of 13 microns SiC powder into AA 2014 alloy) was carried out using the following parameters in a system as shown in the figure:-

(a) Temp. of molten metal = $705^{o}C$

(b) Primary gas - pressure = 0.25 MPa
- flow rate = $0.4 m^3 min^{-1}$
- approx velocity = $240 m sec^{-1}$

(c) Secondary gas - pressure = 0.55 MPa
- flow rate = $6.0 m^3 min^{-1}$
- approx velocity = $300 m sec^{-1}$

(d) Carrier gas SiC loading = $30 kg m^{-3}$

(e) Carrier gas flow rates = $0.03 m^3 min^{-1}$

The product collected consisted of some SiC that did not get incorporated, along with the desired product, which was characterised as follows:-

(a) Composite powder size range = 10-500 microns

(b) Mean size of composite = 80 microns

(c) SiC size range in composite = 6-45 microns

(d) Mean size of SiC in composite = 13 microns

(e) Vol % SiC in the composite powder = 18%

The SiC and Al-SiC composite powders can be separated either by sieving or by gas separation/ classification techniques. An optical section through the composite particles shows comminuted SiC uniformly distributed through the metal matrix.

Example 2

The amount of SiC (or other refractory material) incorporated is dependent on the composition of the Al alloy used and on the atomising conditions. The following table reports the % SiC incorporated in a series of experimental runs performed under the same general conditions as Example 1. The % SiC was determined by sieving the particulate composite to -150 to +38 microns (thereby excluding SiC particles not associated with Al metal), followed by chemical dissolution of the matrix and weighing.

SiC Secondary Atomising Pressure and Mean Diameter

Alloy	Weight % SiC	Volume % SiC	Secondary Pressure	Composite Mean Diam
2014	21.3	18.6	8.0	67.4
6061	28.4	24.8	8.0	68.6
2014	14.5	12.6	7.0	68.8
2014	12.0	10.5	5.3	78.0
2014	17.3	15.1	6.3	70.8
8090	5.5	4.4	5.8	69.2
2014	12.2	10.6	4.7	71.5

Example 3

Two experiments have been conducted both using 2014 alloy and the same powder production conditions as in Example 1. They differ in their processing after the powder production phase.

Experiment A

The as produced powder was sieved to <150μm and then air classified to >45μm producing a composite powder in the size range 45-150μm. The powder was placed in a can (170 mm diameter by 647 mm length) made of 6082 alloy and degassed at 325 C for 4 hours under

vacuum. The can and powder were then hot compacted at 350°C in a commercial press. After cooling the can was machined away.

The hot compacted billet was extruded using an indirect press to a rectangular section 63 mm x 14 mm corresponding to an extrusion ratio of 26:1.

The as-extruded bar was solution heat treated for 1 hr at 505°C, water quenched, and artificially aged for 8 hr at 175°C. Tensile test data was obtained using round bar tensiles machined parallel to the extrusion direction.

Experiment B

The as-produced powder was sieved to <150 m and then air classified to >25 m producing a composite powder in the size range 25-150 m. The powder was placed in a can (74 mm diameter by 200 mm length) made of 2024 alloy. Two degassing conditions were used; 4 hrs at 325°C and 1 hr at 530°C under vacuum. The cans were sealed and then put into a furnace at 300°C for 30 min and then extruded. The extrusion conditions were; container temperature 300°C, billet temperature 300°C, breakthrough pressures <1000 N/mm , ram speed = 12 mm/sec. The extruded cross section was 19 mm round bar corresponding to an extrusion ratio of 15:1.

The as-extruded bar was solution heat treated for 1 hr at 505°C, water quenched, and artificially aged for 8 hr at 175°C. Tensile test data was obtained using round bar tensiles machined parallel to the extrusion direction.

The test results are reported in the following table, together with comparative data on the un-reinforced 2014 alloy. The composites of the invention show higher modulus with no loss of tensile strength.

Property	Experiment A	Experiment B Degassing Temperature 325°C	530°C	2014
0.2% PS (MPa)	430	414.2	442.4	429
TS (MPa)	474	462.7	491.7	476
Ef (%)	3.7	2.3	1.5	7.5
E (GPa)	87	96.0	90.4	73

PS - proof strength
TS - tensile strength
Ef - elongation to failure
E - elastic modulus

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

XXXXXXX
CLAIMS

1. A particulate composite, made by combining molten metal droplets with fine refractory material, in which the particles have a continuous phase of the metal and a disperse phase, incorporated in the continuous phase, of the refractory material.

2. A particulate composite as clained in claim 1, wherein the metal is an Al alloy.

3. A particulate composite as claimed in claim 2, wherein the Al alloy includes at least one transition metal element at least partly in solid solution.

4. A particulate composite as claimed in any one of claims 1 to 3, wherein the particles are spherical.

5. A particulate composite as claimed in any one of claims 1 to 4, wherein the refractory material is an oxide, boride, carbide or nitride.

6. A particulate composite as claimed in any one of claims 1 to 4, wherein the particles have a size in the range 10-500 microns.

7. A particulate composite as claimed in any one of claims 1 to 6, wherein the refractory material is in the form of particles having an average diameter of up to 50 microns.

8. A particulate composite as claimed in any one of claims 1 to 7, wherein the refractory material is uniformly distributed within the particles.

9. A particulate composite as claimed in any one of claims 1 to 8, wherein the continuous phase is of an Al alloy containing a transition metal element selected from 0.5% to 7.0% by weight Cr, 0.5% to 2.5% by weight Zr, and 0.1% to 4.0% by weight Mn.

10. A method of making the particulate composite claimed in any one of claims 1 to 9, which method comprises atomising a stream of a molten metal to form a spray of metal particles by subjecting the stream to

relatively cold inert gas directed at the stream, applying to the stream or spray fine solid particles of a refractory material, allowing the metal particles to solidify, and collecting the resulting particulate composite.

11. A method as claimed in claim 10, wherein the solid particles of refractory material are applied to the stream of molten metal.

12. A solid body formed by compacting the particulate composite of any one of claims 1 to 9.

DATED this 23rd day of September 1987.

ALCAN INTERNATIONAL LIMITED

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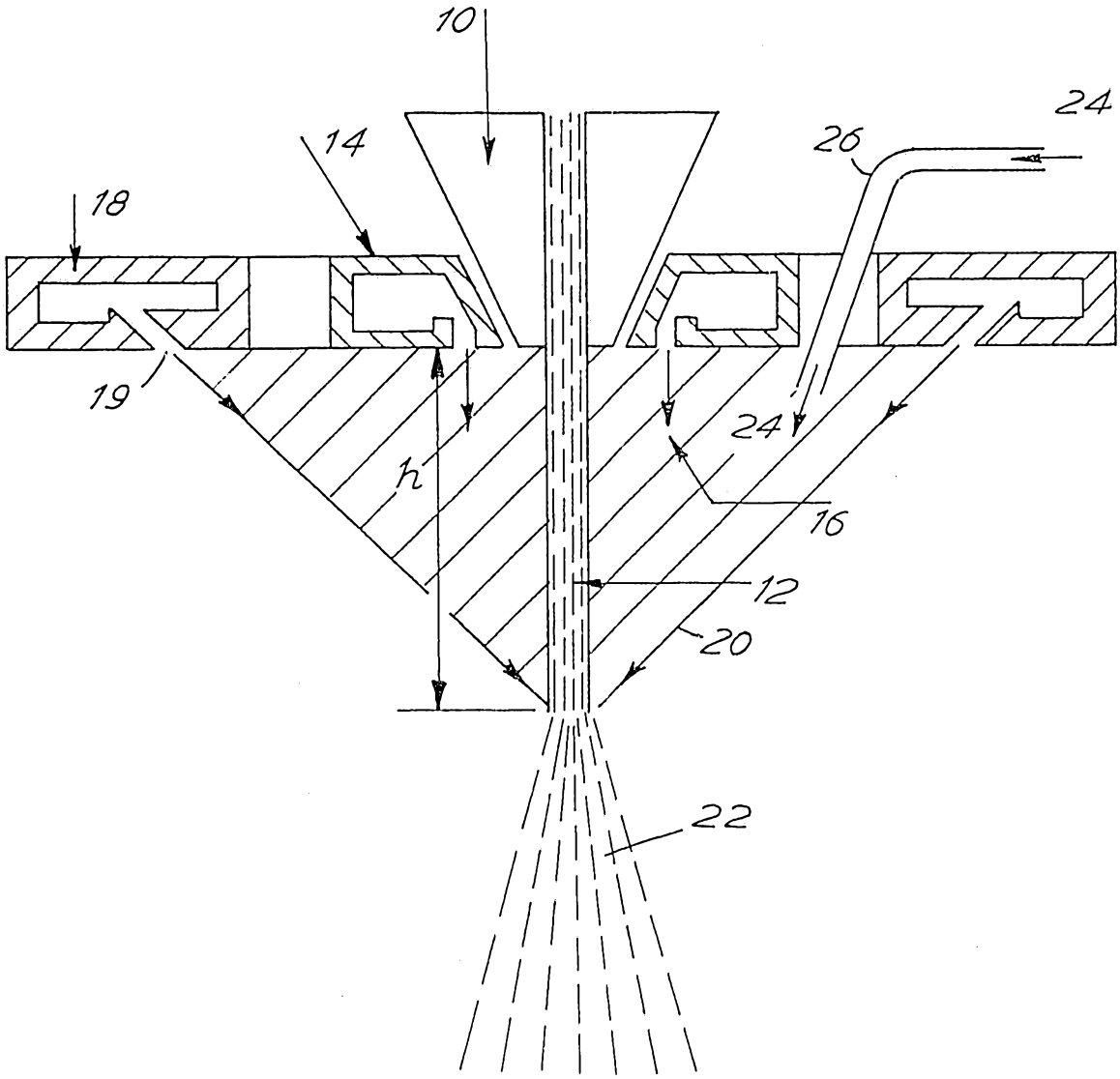


FIG. 1