PRODUCTION OF COMPOSITE METALLIC ARTICLES

Inventors: Frank A. Badia, Ringwood, N.J.; Donald F. MacDonald, Warwick; Frank J. Ansunin, Suffern, both of N.Y.


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Field of Search.................. 75/135, 138, 129, 75/178

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Primary Examiner—L. Dewayne Rutledge
Assistant Examiner—J. E. Legro
Attorney—Maurice L. Pinel

ABSTRACT

Composites formed of incompatible constituents, i.e., constituents which are mutually insoluble, are produced by introducing at least one such constituent in coated form into a molten bath of the other, the bath being subjected to the influence of a vortex.

25 Claims, No Drawings
PRODUCTION OF COMPOSITE METALLIC ARTICLES

As those skilled in the art are aware, there are any number of "metallurgically incompatible systems" in which one constituent is, as a practical matter, virtually completely insoluble in another. The aluminum-graphite system is rather exemplary for upon mixing graphite into molten aluminum the graphite is rejected from the melt, i.e., the graphite all too quickly floats to the melt surface, the body of molten aluminum (and ultimate solidified product as well) being conspicuous by the absence of any significant percentage of retained graphite. As has been observed, so complete is this non-reactivity that graphite boats are used in zone refining (purifying) aluminum, there being such little fear of graphite contamination.

Now, it would be of considerable advantage if this inherent metallurgical incompatibility phenomenon could be negated for it follows that in countless situations the introduction of one such constituent into another could afford the opportunity, depending upon the nature of the constituent, of achieving various desired mechanical, physical or other characteristics found wanting in the other. One might cite, by way of example, the frictional qualities contributed by graphite in aluminum, the improved hardness and strength imparted by aluminum oxide in aluminum or copper, the enhanced abrasive qualities conferred by the presence of silicon carbide or silicon dioxide in aluminum and zinc alloys, etc.

Recently, a significant breakthrough was scored in respect of this historically old problem. In its preferred embodiments and again using graphite-aluminum for purposes of illustration, it was found that quite satisfactory retention and dispersion of graphite in aluminum obtained when graphite powder was metal-coated (e.g., with nickel) and then introduced into molten aluminum in conjunction with a gaseous stream such as nitrogen. An important consideration was that in using metal coatings the metallic character thereof had to be substantially preserved, e.g., to prevent oxidation, at least until the coated particles were introduced into the body of the melt. The present invention is addressed essentially to the same problem but a new and different process has been developed, a process which among other advantages, can be carried forth both more expeditiously and economically, and which in many instances does not require special measures to ensure against oxidation attack.

Generally speaking, the present invention concerns the pyrometallurgical production (melt processing as opposed to powder metallurgy) of composite metallic products ("composites") characterized in that at least one constituent thereof (often referred to herein as the "dispersed") is, as a practical matter, insoluble in a second, the latter being metal the percentage of which (by volume) is less than that of any other component of the composite. Compositions containing a plurality of ingredients as well as those of the binary type are contemplated as will be evident hereinafter, i.e., the second constituent can be an alloy or a single element.

In accordance herewith, it has been found that by subjecting a molten bath of metal in which the desired dispersed constituent is normally insoluble to the influence of a vortex and introducing therein a plurality of the dispersed particles, the surfaces of which are substantially enveloped by a coating, composite products can be produced containing a very significant and highly useful percentage of the dispersed. In this connection, the coated particles can be added before or after generating the vortex or during the generation thereof. In any case, the melt is thereafter suitably solidified whereupon the composite can be further processed, if desired, e.g., as by hot working to produce wrought products.

In carrying the invention into practice the dispersed particles may take the form of powders, pellets, fibers, etc., the specific property required and/or the intended application usually being a determining factor. For example, powders would be likely used where such qualities as friction, abrasion and wear are important whereas fibers would often be useful where enhanced strength would be the primary objective. Powders sub-micron in size can be utilized although sizes on the order of about 5 or 10 microns or more might be more conducive to ease of handling.

The coatings encapsulating the dispersed in advantageously metallic. Metals such as nickel, copper, cobalt, iron, aluminum, zinc and various alloys thereof are deemed suitable. Among other useful metals might be mentioned silicon, tin, molybdenum, chromium, antimony and tungsten. The coating should possess the capability of imparting or contributing to achieving a state of wettability between the incompatible materials sufficient to cause or bring about the dispersion and retention of one in the other. It is considered preferable in using metal coatings that the metal selected not be one capable of readily forming a substantial solid solution with the base material, e.g., nickel in copper. With coatings which form solid solutions it is thought that the initial condition of wettability might not be retained for as long a period of time as where the coating reacts with the base material to form, say, an intermetallic compound, e.g., nickel in aluminum. As a consequence, a higher loss in retained dispersed particles from rejection of the melt could be expected together with poorer dispersed distribution.

In striving for best results, the coating should envelop the dispersed surface as completely as possible. Since the overall enclosed surface area is significantly less than what otherwise could be attained, greater can be the expected loss percentagewise of retained (recovered) dispersed in the incompatible component, a point being ultimately reached at which recovery of the dispersed is so inferior as to be tantamount to virtual rejection. This is simply another way of stating that poor coatings lead to inferior results.

Mention perhaps should be made that though a particular coating is suitable for use in introducing the dispersed, its presence might detract from the final product in some respect. Therefore, some attention should be given aforesaid as to the likely effect of the coating material in the ultimate product. To what extent coating thickness may not be of significant importance in many instances, excessive thicknesses might introduce into the final product an amount of the coating constituent beyond desirable limits for the purpose intended. Coating thicknesses up to 25 or 50 microns are ordinarily satisfactory. And in this connection, the coatings can be provided by well known procedures, including galvanic deposition, deposition from decomposition of carbonyls, e.g., nickel from nickel carbonyl, etc.
With regard to the vortex induced in the molten baths, the energy used to generate the vortex should be sufficient to overcome the surface tension at the melt surface such that the vortex is visible. Excessive speeds to the point of turbulence are without benefit and may lead to the loss of material by way of overflow or to undue oxidation of the bath or to the introduction of an undesirable amount of dross in the melt body. On the other hand, unnecessarily low speeds could result in sluggishness of operation with attendant inferior results. For example, although the use of speeds in which a visible vortex is not induced are not excluded from the invention, a greater amount of processing time is more apt to be required and the percentage of retained dispersoid particles might be less. As to other considerations, mention might be made that the rotational speed employed in a given case will somewhat depend upon the nature of the particular materials used in forming a composite, as will be appreciated by those skilled in the art. Generating a vortex in aluminum (light) and lead (heavy) might, though not necessarily, require different speeds due, for example, to viscosity effects. Too, where an impeller is used the diameter thereof will also have an influence upon impeller speed.

As a distinct practical advantage of the subject invention, it is further contemplated that the production of multiple successive castings, e.g., aluminum die and permanent mold castings, can be considerably facilitated. Thus, after introduction and dispersion of the dispersoid particles are complete the speed rather than being discontinued can be reduced to a level which promotes the retention of the suspended particles while at the same time pouring of successive castings is conducted. Accordingly, prolonged holding periods (as evident from the 20 minute period in Example 1) can be employed without undue detriment. The use of an impeller to control the speed lends itself to such operations.

Apart from the use of an impeller, the vortex can be created by other known suitable means, including other mechanical devices or by techniques such as those involving magnetic principles.

For the purpose of giving those skilled in the art a better appreciation of the invention, the following illustrative examples and data are given.

**EXAMPLE I**

A 50 lb. heat of an aluminum-base alloy (nominally containing 9 percent silicon, 3 percent copper and 1 percent magnesium, the balance essentially being aluminum) was melted in an induction furnace fitted with a clay-graphite crucible. The melt was brought to and maintained at a temperature of about 1,350°F. and then degassed with nitrogen for approximately 10 minutes. (In commercial practice aluminum and aluminum-base alloys are commonly degassed with nitrogen and this step was for the purpose of simulating commercial processing.) A four-bladed impeller was placed in and near the bottom of the bath, the shaft being inclined about 20 degrees from the vertical. About 5 lbs. of nickel-coated graphite particles ranging in size from about 100 to 325 mesh (U.S. Series Equivalent) were then dispersed on the melt surface and a visible vortex was induced in the bath by rotating the impeller (driven by an air motor) at approximately 520 revolutions per minute (rpm.).

As a result of the influence of the vortex, the coated particles (each coated particle contained about 50 percent nickel and 50 percent graphite, 2.5 lbs. of graphite being added) were drawn down and into the molten bath within a period of about 1 minute. The impeller speed was then reduced to 70 rpm. From a visual observation, the vortex had disappeared but no marked rejection of graphite was noted at the surface.

With the impeller still running at 70 rpm., 6 permanent mold slab castings (1 1/4 x 4 x 4 inches) were poured using a hand ladle to transfer the molten metal to copper chill molds. The first three were cast in succession, the second group of three being cast after holding the melt at temperature for a 20 minute period. Metallographic examination indicated that the graphite was dispersed relatively uniformly throughout the castings. Graphite recovery was quite good, averaging about 88 percent.

**EXAMPLES II – VI**

Using the same general techniques as described in Example I, graphite was also successfully introduced and retained in molten baths of aluminum, zinc and a zinc-aluminum alloy nominally containing 4 percent aluminum (Zn-4Al), all of commercial purity. In addition to nickel, coatings of copper (35 percent Cu-65 percent graphite by weight) and iron (50 percent Fe-50 percent graphite) were also used. The aluminum melts were about 1.9-2 kilograms (kg.) whereas the zinc and Zn-4 Al melts were approximately 4.5 kg. When the impeller speed was reduced to the 70 rpm. level, it was held therefor for about 5 minutes before pouring (hand ladle) into copper permanent molds (1 1/4 x 4 x 7 inches). The results are reported in Table I.

<table>
<thead>
<tr>
<th>Base Melt</th>
<th>Type of Coated Dispersoid</th>
<th>Added</th>
<th>Weight % Dispersoid Analyzed</th>
<th>Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>50% Ni-50% graphite</td>
<td>2.63</td>
<td>2.2</td>
<td>78</td>
</tr>
<tr>
<td>Zn</td>
<td>50% Ni-50% graphite</td>
<td>0.98</td>
<td>0.63</td>
<td>64</td>
</tr>
<tr>
<td>Zn-4 Al</td>
<td>50% Ni-50% graphite</td>
<td>0.98</td>
<td>0.88</td>
<td>89</td>
</tr>
<tr>
<td>Al</td>
<td>35% Cu-65% graphite</td>
<td>1.85</td>
<td>1.47</td>
<td>79</td>
</tr>
<tr>
<td>Al</td>
<td>50% Fe-50% graphite</td>
<td>1.03</td>
<td>0.65</td>
<td>63</td>
</tr>
</tbody>
</table>

Examination of the castings reflected that the graphite distribution was good, a result indicative that a variety of different coatings can be employed.

That dispersoids other than graphite can be introduced, dispersed and retained in various molten baths of incompatible base materials is illustrated by Example VII.

**EXAMPLE VII**

Using the procedure set forth in Examples II–VI, approximately 0.98 percent of silicon carbide was introduced in the form of nickel-coated particles (50 percent nickel by weight) into an aluminum-base alloy melt which nominally contained 12 percent silicon. Subsequent metallographic examination revealed a uniform dispersion of silicon carbide throughout the alloy matrix and analysis showed the presence of about 0.88 percent silicon carbide, a recovery of some 89 percent.

As indicated above herein, an advantage of the subject invention is that in using metal coatings the undertaking of special precautionary measures to protect the coatings from atmospheric attack is normally not necessary before being subjected to the influence of the
3,753,694

vortex action. This is demonstrated by the results described in connection with Example VIII.

EXAMPLE VIII

After forming a molten bath (50 lb.) of a composition set forth in Example I, approximately 5 lbs. of nickel-coated graphite (50 percent graphite) were dispersed on the surface of the melt and permitted to dwell thereon for about 35 minutes at which point the impeller was turned on and the speed raised to 520 rpm., thus generating a visible vortex. After the lapse of about 2 minutes, the impeller speed was reduced to 70 rpm. as in Example I. Again, the once visible vortex disappeared and no marked rejection of graphite was visually detected. Ten permanent mold castings were poured consecutively as in Example I and upon examination each exhibited a pattern of satisfactory graphite distribution, notwithstanding the dwell time of 35 minutes. Three of the castings were analyzed for graphite recovery and the average percentage retained was about 78 percent.

EXAMPLE IX

In a further test performed in much the same manner as in Example VIII, a determination was made that during the dwell period nickel oxide formed. In this test a dwell time of 15 minutes was used; however, samples of the nickel-coated graphite particles were removed at predetermined time intervals of 1 min., 2½, 5 and 15 mins. Temperature was maintained at about 1,350°F. Upon X-ray diffraction analysis, a nickel oxide phase was detected as well as nickel and carbon, the intensity of the oxide (ratio of nickel oxide to nickel) increasing with dwell time. (A control example showed only nickel and carbon.) After the 15 min. period, the remaining nickel-coated graphite particles were subjected to the vortex treatment with good results.

The fact that the coated dispersoid particles can remain on the surface of a molten bath for a period at least sufficient for a reaction to take place whereby a substantial portion of the surface of the coating assumes the oxide form but without ultimate detrimental results, is advantageous from a commercial viewpoint. Apart from rendering special measures unnecessary, should an operator unduly delay in generating the vortex once coated particles have been deposited on the melt surface, the operation need not be stopped and scrapped with the possible incurrence of added expense through loss of material, downtime, etc.

It should be pointed out that at least one or more of the constituents constituting the base metal should be capable of reducing the surface of the coating if in oxide form. It is believed that when the oxide is pulled down into the cavity and into the body of molten metal, during the period of suspension therein it is reduced by or reacts with the molten metal such that it transforms back into its native (metallic) state to an extent sufficient to impart substantial compositional stability between the otherwise incompatible materials. Put another way, it is thought that the vortex operation allows for adequate suspension time to enable the reduction process to take place to a substantial degree. If the molten base metal is incapable of reducing the oxide form of the coating, it is deemed advantageous to protect the metal-coated particles with a protective atmosphere, i.e., a gas blanket, e.g., nitrogen or argon, during the introduction of the coated particles into the bath.

Among other incompatible systems envisaged as being treatable in accordance herewith, are graphite in copper and copper alloys (e.g., brass and bronze) and lead and tin alloys; silica, alumina and magnesia and other oxides in metals such as copper and nickel; silica, magnesia and others in aluminum; heavy oxides in lead; silicon carbide in nonferrous metals as, for example, zinc or copper as well as aluminum; diamond in aluminum and zinc among others; mica in low melting point metals as zinc, lead, aluminum and magnesium; etc. Nitrates and borides as well as carbides and oxides can also serve as the dispersoid. For improved lubricity, molybdenum disulfide is considered a useful dispersoid. Also contemplated are intermetallic compounds.

In addition to obtaining such characteristics as improved frictional qualities, wear and abrasion resistance and increased strength, such other properties as machinability, corrosion resistance and magnetism can also be achieved depending, of course, upon the nature of the particular composite desired. Composites having the attributes of a particular color or colors can also be produced. This would have the advantage of providing "through color composites" as distinct from color only on the surface which might be easily removed through scratching, wear etc. In this connection the coating should not decompose i.e., should be stable, at the melt temperature. Moreover, composites possess the ability to provide "dampening capacity" and this would be useful for noise abatement. Actually, properties can be changed or altered in accordance herewith in a manner not permitted by conventional alloying.

Among the host of articles of manufacture that might be formed from composites produced in accordance herewith are sliding contact elements such as pistons, bearings, sliding valves, cylinder liners and blocks, electrical pickup shoes, all of which can be made from composites of graphite in aluminum and aluminum alloys. Non-skid devices such as tread plates, boat seats, tool handles, boot and shoe soles, nails, etc. are contemplated. So too are friction generating devices (discs, brakes, brake drums, linings and the like); friction drive components (clutches, conveyor belts, conveyor rolls, gears, mechanisms for toys and projectors, pulleys for belt drives, etc.); machine tool equipment (laps, hone, broaches, dies, tools, etc.); and abrasion resistant materials (electrical contacts, e.g., for switch gears, pump casings, safes, heat and drill proof items, and grinding wheels). The production of gears, high strength engineering members and decorative articles are also within the scope of the invention.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations can be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. A process for producing a solid composite metal product having a metal matrix and at least one constituent distributed therein which is virtually insoluble in a molten bath of the matrix metal, which comprises forming a melt of the matrix metal, supplying energy from an external power source to the molten bath such that the molten metal is caused to rotate at a speed sufficient to overcome the surface tension of the melt and
to induce therein a visible vortex, subjecting particles of the said insoluble constituent to the rotational action of the vortex, the surfaces of the insoluble constituent particles being substantially encapsulated by a coating possessing the capability of imparting a condition of wettability between the particles and the molten metal, maintaining the vortex until the particles are introduced into and dispersed within the body of the molten bath, and thereafter solidifying at least a portion of the molten metal.

2. A process in accordance with claim 1 in which prior to solidifying molten metal the rotational speed of the bath is reduced and while simultaneously maintaining the insoluble constituent particles suspended therein portions of the molten bath are successively cast.

3. A process in accordance with claim 1 in which the coating is metal.

4. A process in accordance with claim 3 in which the coating is selected from the group consisting of nickel, copper, iron, zinc, cobalt, aluminum and alloys thereof.

5. A process in accordance with claim 1 in which the constituent is selected from the group consisting of graphite, oxides, carbides, nitrides and borides.

6. A process in accordance with claim 3 in which the constituent is selected from the group consisting of graphite, oxides, carbides, nitrides and borides.

7. A process in accordance with claim 6 in which at least graphite is present.

8. A process in accordance with claim 6 in which the coating is selected from the group consisting of nickel, copper and iron.

9. A process in accordance with claim 7 in which the coating is selected from the group consisting of nickel, copper and iron.

10. A process in accordance with claim 9 in which the matrix is aluminum or aluminum alloy.

11. A process in accordance with claim 10 in which the coating is nickel.

12. A process in accordance with claim 8 in which the coating is selected from the group consisting of nickel, copper, iron and zinc.

13. A process in accordance with claim 8 in which the matrix metal is from the group of aluminum, aluminum alloys, zinc and zinc alloys.

14. A process in accordance with claim 13 in which the coating is nickel.

15. A process in accordance with claim 7 in which a piston is cast, the matrix metal being aluminum or aluminum alloy.

16. A process in accordance with claim 15 in which the coating used is from the group of nickel, copper, iron and zinc.

17. A process in accordance with claim 25 in which the article is a sliding contact element.

18. A process in accordance with claim 17 in which the sliding contact element is a bearing.

19. A process for producing a solid composite metal product composed of at least one dispersoid constituent distributed therein which is virtually insoluble in a molten bath of the metal, which comprises forming a melt of the matrix metal, supplying energy to the molten bath such that the molten metal is caused to rotate at a speed sufficient to induce therein a vortex, subjecting particles of the insoluble dispersoid to the action of the rotational effects of the vortex, the surfaces of the particles being substantially encapsulated by a coating possessing the capability of imparting a condition of wettability between the particles and the molten metal, maintaining the vortex such that the particles are drawn into and dispersed within the body of the molten bath, and thereafter solidifying at least a portion of the molten metal.

20. A process in accordance with claim 19 in which the energy supplied is sufficient to overcome the surface tension at the melt surface.

21. A process in accordance with claim 20 in which the coating is metal.

22. A process in accordance with claim 21 in which the metal coating is incapable of readily forming a substantial solid solution with the base metal.

23. A process in accordance with claim 21 in which the base metal is capable of reducing the surface of the coating when in the form of an oxide.

24. A process in accordance with claim 21 in which the metal coated dispersoid particles are substantially protected by a protective atmosphere during the introduction thereof into the bath.

25. A process for producing a solid composite metal product member selected from the group consisting of a sliding contact element, a non-skid device, a friction generating device, a friction drive component and an abrasion resistant article, which comprises forming a matrix of molten metal, supplying energy from an external power source to the molten bath such that the bath is caused to rotate at a speed sufficient to overcome the surface tension of the melt and to induce a visible vortex therein, introducing into the molten bath particles of at least one constituent virtually insoluble in the molten metal, the said insoluble constituent particles being subjected to the action of the rotational effects of the vortex and being further characterized in that they are substantially encapsulated by a metal coating possessing the capability of imparting a condition of wettability between the particles and the molten metal, maintaining the vortex until the particles are introduced into and dispersed within the body of the molten bath, solidifying the molten metal into a composite body and then forming the solid composite into the metal product member desired.
UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION  

Patent No. 3,753,694  
Dated August 21, 1973  

Inventor(s) Frank Arthur Badia, Donald Francis MacDonald & Frank Joseph Ansuini  

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:  

Claim 1, line 1, cancel "for" and insert -- capable of--  
Claims 5, 6 and 8, line 2 of each, before "constituent" insert "insoluble";  

Claim 10, line 2, after "matrix" insert "metal";  

Claim 19, line 1, delete "for" and insert "capable of";  

Claim 25, line 1, delete "for" and insert "capable of".  

Signed and sealed this 23rd day of July 1974.

(SEAL)  
Attest:  
McCoy M. Gibson, Jr.  
Attesting Officer  
C. Marshall Dann  
Commissioner of Patents