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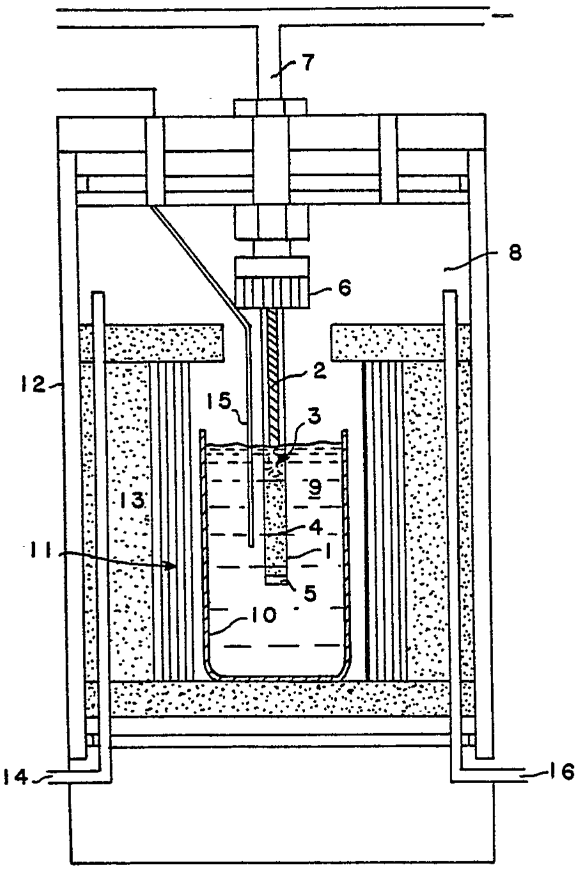
(54) Solid composite material particularly metal matrix with ceramic dispersates.

(57) Composites of materials in which the matrix material does not spontaneously or readily wet the disperse phase and in which the volume fraction of the disperse phase is less than that formed in a packed bed of dispersate particles can be made effectively by an indirect method of infiltrating a packed bed of dispersate particles, using pressure or other mechanical force as needed to overcome poor wetting and form an intermediate concentrated composite. The concentrated composite is then mixed with additional matrix-forming material to produce the finally desired composite. The technique is particularly valuable for composites with ceramic dispersates and metal or alloy matrixes. When the matrix is predominantly aluminum and the dispersates are predominantly silicon carbide, a barrier coating of a material that retards reaction between silicon carbide and alumina is useful.

FIG. 1



This invention relates to solid composite materials, preferably metal-matrix composites (MMC), which comprise a continuous metal matrix material having a plurality of separate particles, i.e. dispersates, dispersed throughout the matrix and to methods for making such composites having an extremely uniform dispersion of the dispersates and simultaneously having essentially no porosity. The invention is particularly directed to metal-matrix composites having ceramic dispersates substantially uniformly distributed throughout the matrix phase. The present invention provides a solution to the problems of excessive porosity in the MMC's and excessive clustering of the particulates, which problems have prevented as-cast composites from having properties comparable to powder metallurgically forged or extruded composites.

It is well known that composite materials often have better mechanical properties than either the matrix or the dispersates alone. The extent of the improvement in properties has generally been found to be a function of the degree of distribution of the dispersates. However, making composites with reproducible and extremely uniform dispersions of dispersates has proved extremely difficult.

One method of making composites in which a matrix material is obtained from a fluid state is to disperse dispersates in a precursor liquid and then form the composite by solidifying the liquid part, i.e. dispersion medium, of the dispersion. In practice, however, it has been quite difficult to perform due to density differences which normally are present between the dispersates and the dispersion medium. These differences generally lead to a non-uniform distribution of the dispersates in not only the liquid dispersion, but also the final composite.

U.S. Pat. No. 4,735,656 suggests overcoming the density segregation problem by (i) mixing metal particulates with ceramic particulates and then (ii) heating the mixture to a temperature high enough to cause partial melting of the metal (so that it fuses into a dense matrix when cooled) but not so high as to cause the ceramic particulates to float therein. The care required to utilize this process makes the process undesirable for large scale commercial operations. Also process does not inherently preclude the presence of voids in the final product.

Another problem with using the simple mixing concept is that many of the most desirable dispersates are difficult to wet by known fluid precursors of desirable matrix phases. Int. Pat. Appln. WO 87/06624 teaches the use of specific dispersing and/or sweeping impellers to promote high shear mixing while minimizing the introduction of gases into the mixture as well as the retention of the gases at the interfaces of the dispersates and the matrix material. U.S. Pat. No. 4,662,429 teaches the addition of lithium to an aluminum matrix alloy melt to facilitate wetting and dispersing of the dispersate in the matrix alloy. European Pat. Appln. No. 87 201512.8 describes composites of a zinc-aluminum alloy reinforced with silicon carbide powder which "surprisingly" has good mechanical properties without the difficulties often experienced with other similar composites.

The difficulties in making good quality composites, and some of the methods attempted for dealing with the problems are generally reviewed in "Solidification, Structures, and Properties of Cast Metal-Ceramic Particle Composites," P.K. Rohatgi et al., 31 International Metals Reviews 115-39 (1986). One method, described in more detail by B. C. Pai et al., 13 Journal of Materials Science 329-35 (1978), involves pressing together dispersates with powdered matrix material to form a pellet, introducing the pellet with stirring below the surface of the fluid matrix precursor material for a sufficient time both to melt the pellet and to disperse the dispersates within the total amount of fluid precursor material, and then solidifying the dispersion. Analogously, J. Cisse et al. in 68 Metallurgical Transactions 195-97 (1975) describe the use of a "master alloy" of sintered aluminum powder rods which contain 10 w/o aluminum oxide.

A. Mortensen et al., Journal of Metals, February 1988, pp. 12-19, also reviews the field and refers to Rohatgi et al. as listing a number of techniques for introducing particulates, including pre-infiltrating a packed bed of particulates to form a pellet or "master alloy" and redispersing and diluting it into a melt of a matrix material or its precursor.

All of the prior art methods initially produce composites which contain substantial porosity unless the dispersates are easily wet by the fluid matrix material. And if the dispersates are easily wet, the subsequent properties of the composite are often degraded as a result of chemical reactions which occur between the matrix material and the dispersates.

It is therefore an object of this invention to produce composites containing as little porosity as possible. It is a further object to minimize the time required to make the composites so that chemical degradation of the dispersates by the final matrix material or a precursor thereto in the composite is precluded or at least substantially minimized.

SUMMARY OF THE INVENTION

Composites having the most desirable properties for many purposes are produced when the dispersates therein are sufficiently widely dispersed that most of them do not touch another dispersate particle. This class of composites is characterized herein as having "discrete" dispersates or as a "discrete dispersion." It has now been found that many of the difficulties in the prior art of making discrete composites can be overcome by using an indirect method of preparation which entails (i) making a concentrated dispersion of dispersates and a precursor to the final matrix in which there is intimate contact between the precursor matrix material and the dispersates and then (ii) dissolving the concentrated dispersate dispersion in additional matrix precursor material.

Thus in the present invention a concentrated dispersion is used to form the more dilute dispersion of the disired composition by mixing it with additional matrix fluid precursor and dispersing it therein. If the mixing is done while the dispersion medium of the concentrated dispersion is still fluid, this embodiment is referred to as a "continuous" method. Sometimes, however, it may be more convenient to solidify the dispersion medium of the concentrated dispersion producing a "concentrated composite" before beginning the mixing step to prepare the finally desired composite. Composites made in this way are denoted as being made by the "concentrated composite" embodiment of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-section view of one type of apparatus useful in the practice the instant invention.

Figures 2-3 and 6-7 are cross sections of composites produced according to the invention or of comparison composites.

Figures 4 and 5 are cross-section views of another type of apparatus useful for the practice of this invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that satisfactory concentrated disper sions according to this invention can be made by packing dispersates into a porous bed in which most dispersates touch at least one other dispersate, and then infiltrating the packed bed with a fluid precursor to the desired final matrix such that (i) the reasonably uniform distribution of dispersates characteristic of the packed bed is maintained during the infiltration and (ii) most, if not all, of the gas existing in the interparticle volume of the bed is displaced during the infiltration step. In this way, the infiltrated packed dispersate bed becomes a concentrated dispersion of dispersates useful in this invention. Preferably the concentrated dispersion will have no more than about five volume per cent voids and/or gases. Still more preferably, porosity is substantially entirely eliminated from the concentrated composite. Dispersions having these characteristics are made having higher concentrations of dispersates than is normally desired in the final product.

If the packed porous bed of dispersates is evacuated before infiltration, the fluid infiltration into the bed may be accomplished from multiple directions, if desired. Often it is more convenient to omit the evacuation step and infiltrate the dispersate bed only from a single direction while permitting the displaced air to escape through an open part of the bed. When the fluid precursor does not spontaneously wet the dispersates, infiltration may still be successsfully achieved by applying a pressure to the fluid. Although the infiltration process generally does separate some of the interparticle contracts between the packed dispersates, the resultant dispersion is more concentrated than the final dispersion made therefrom.

The infiltration of the packed porous bed of dispersates is usually performed under minimum suitable conditons of both temperature and pressure. By using a low temperature, any reaction between the dispersate powder and the matrix precursor will be minimized. Thus the temperature of the matrix precursor fluid used should be about 25 to about 200, preferably about 50 to about 175, and most preferably about 75 to about 125° C. above its melting point. Preferably the dispersates are preheated to essentially the temperature of the matrix precursor fluid to prevent metal cooling or freezing off which otherwise could occur and reduce or prevent the complete infiltration. With regard to pressure, the use of pressure has been found to be advantageous to reduce/eliminate porosity in the concentrated dispersion but simultaneously increase the cost of performing the infiltration. Thus the pressure used is chosen to balance the level of porosity of the concentrated dispersion and the cost. Generally, an overpressure of at least 25 psi will be preferred with still higher overpressures being more preferred as the particle size of the dispersates is reduced. Also to help minimize any porosity due to too low a pressure having been used, it has been found to be desirable to increase the overpressure to about 200 to 300 psi near the end of the infiltration process.

In order to promote good displacement of interparticle gases at relatively low infiltration pressures during the formation of the composites, it has been found beneficial to incorporate known wetting agents to the matrix precursor materials used to form the concentrated dispersion. The specific wetting agents and amounts thereof utilized will normally depend upon the specific matrix material and dispersate and can be determined by routine experimentation. For instance, when preparing a composite of silicon carbide and an aluminum alloy, tin and potassium hexafluorozirconate are preferred wetting agents since they are known to promote the wetting of silicon carbide and can be readily added to the aluminum alloy precursor material.

The mixing of the concentrated dispersion with additional precursor fluid is then accomplished in a way that avoids the difficulties with dispersing small particles directly in an open container of fluid, as discussed above. With the favorable concentrated dispersions of this invention, mixing becomes very easy. Portions of the concentrated dispersion can simply be placed atop a second matrix fluid, if the dispersates are denser than the matrix, or covered with the second matrix fluid, if the dispersates are less dense than the matrix. A combination of gravity and stirring then mixes the dispersates into the total amount of fluid matrix precursor. It has been found that concentrated dispersions made by the methods described herein often have the very favorable property that, at some temperatures, they behave as if the dispersates were so well bonded to the matrix that each dispersate tends to carry a substantial amount of matrix material with it when moved.

Preferably a non-vortex generating mixer will be used to minimize any air entrapment. The mixer must obviously be made of a material which will not react with or degrade the matrix precursor fluid. Suitable such materials will depend upon the particular composition of the composites. For example, with an aluminum alloy matrix, mixers prepared from graphite or steel coated with a nonwetting wash or spray such as carbon, sodium chloride, or mica wash are preferred. In some alloys, Cotronics 902 machinable ceramic from Contronics Co., Brooklyn, NY, may be used.

High shear mixing is preferred to disperse any small clusters or agglomerates of dispersates remaining from the concentrated dispersion and also to provide a more uniform distribution of the dispersates in the final composite. During mixing, the temperature is normally maintained within the range at which the mixtures containing the dispersates exhibit thixotropy so that efficient mixing is achieved while reducing the possibility of dispersate resegregation due to density differences as the mixed material moves away from the mixing zone.

Certain procedures for accomplishing the mixing step have been found either convenient or preferred. In performing the continous embodiments of the invention, as shown in Examples 9 and 10 below, it is often convenient to provide a pressurizable reservoir of the concentrated dispersion from which it is injected into at least a portion of the second precursor fluid. To facilitate mixing, it is generally preferred to inject the concen trated dispersion into a flowing stream of the second precursor fluid. For the concentrated composite embodiment, for which Example 1 below describes a suitable apparatus, a portion of the concentrated composite may be held mechanically below the surface of a body of second precursor fluid, maintained at a temperature high enough to reliquify at least part of the matrix of the concentrated composite, and portions of the two components of the concentrated composite can be mixed into the second precursor fluid as liquefication occurs. Alternatively, the concentrated composite can be heated to, and held at, a temperature sufficient for partial liquefication of its matrix, and additional fluid precursor added with mixing.

One aspect of this invention is the final composites produced. The invention provides the first discrete dispersions that are (i) substantially free of pores and (ii) have an essentially uniform dispersion of the dispersates. In particular, new dispersions and also not more than about 40 volume percent of dispersates and also not more than about 5 volume percent voids, pores and gases are provided herein.

In connection with this invention, it should be understood that a "precursor of a matrix material" refers to any material that can be converted into the desired matrix material by chemical or physical treatment without dislocation of any dispersates contained therein. Thus, a liquid alloy or a thermoplastic resin is a precursor to the solid alloy or resin into which it hardens on cooling; or fluid mixtures of polyfunctional isocyanates and polyfunctional alcohols are precursors to the polyurethanes that they form by chemical reaction after mixing; or fluid acrylated materials are precursors of the polymer that they form after exposure to an electron beam. "Matrix" is used herein to refer to the continuous phase of any dispersion or composite, be it in a fluid or a solid state.

The solid composite materials of the present invention are comprised of two primary materials - the matrix and the dispers ates. Matrix materials useful in the present invention include metals, metal alloys, and thermoplastic resins. Suitable metals and metal alloys include aluminum, aluminum alloys, magnesium, magnesium alloys, bronze, copper, copper alloys, zinc, and zinc alloys. Suitable thermoplastic resins include polyester polyurethanes, polyether polyurethanes, and acrylic polymers and copolymers. Preferably the matrix material is selected from aluminum, aluminum alloys, magnesium, magnesium alloys, and magnesium-aluminum alloys. Most preferably the matrix material is an aluminum alloy containing less than about 12 w/o, preferably less than about 8 w/o, and most preferably less than about 1.5 w/o silicon.

Suitable dispersates for use herein are ceramic materials such as silicon carbide, silicon nitride, aluminum nitride, alumina, titania, silica, boron carbide, borides, carbides, silicides, diamond and the like. These materials are characterized as having a modulus, strength and wear resistance which are substantially higher than that of the matrix materials. Preferably the dispersates are either silicon carbide, silicon nitride, aluminum nitride, or aluminum oxide. Most preferably the dispersates are silicon carbide. The dispersates, irrespective of the particular chemical composition, are used in the form of fine particles, generally having an average particle size of about 0.1 to about 45 microns, preferably about 3 to about 20 microns, and most preferably about 7 to about 15 microns.

The concentrated dispersion will generally be prepared to contain as much dispersate as possible. Thus, about 25 to about 85 w/o, preferably about 45 to about 60 w/o, and most preferably about 53 to about 56 w/o dispersates will be used.

Some of the most useful applications of this invention are in the manufacture of composites of silicon carbide dispersed in aluminum or magnesium alloys. Such materials are valuable construction materials for applications such as airplane bodies and other components in which a combination of low density, high toughness, and high flexure resistance at temperatures not too far below melting point of the alloy are needed. Previously it had been very difficult to make composite products having about 20 w/o silicon carbide, the most mechanically desirable range, with the substantially uniform dispersion of silicon carbide particles that is needed. This was particularly true when the silicon carbide particles were mostly less than ten microns in size and/or had a wide distribution of sizes. Such composites can be readily produced with the present invention.

Alloys of aluminum containing from about 1 to 4% silicon are known to make stronger composites when reinforced with ceramic materials such as silicon carbide than do aluminum alloys containing less silicon. This is so even though unreinforced silicon-aluminum alloys containing less than 1% silicon are stronger than those containing more than 1% silicon. The difficulty of making composites with low-silicon aluminum alloys and silicon carbide is believed caused by a reaction between the low-silicon aluminum alloy and the silicon carbide dispersates which produces aluminum carbides. The aluminum carbide formation weakens the matrix/particulate interface and makes SiC a less effective reinforcement material.

Similarly, when silica dispersates are used with a low-silicon aluminum alloy they can react with the aluminum to form silicon and alumina. And when titania dispersates are utilized to reinforce low-silicon alloys, they can react to from Ti º Al and alumina. Similarly, other deleterious reactions can occur with various ceramic and metal combinations, as is known.

The difficulties caused by such deleterious interactions between desirable dispersates and either the precursor to the matrix material or the matrix material itself, such as occur when silicon carbide dispersates are used to reinforce a low-silicon aluminum, can be overcome with an embodiment of the present invention. The deleterious reaction is inhibited sufficiently, or ideally prevented, by coating the dispersate particles with a material that (i) will not react with either the precursor or the matrix material, but (ii) will produce an adherent coating on the dispersates, and (iii) will promote wetting of the dispersates by the matrix precursor.

Suitability of particular dispersate coating materials can be determined by routine experimentation by coating particular dispersates, then attempting to infiltrate a packed porous bed thereof with the desired matrix precursor fluid, and if the infiltration succeeds then attempting to disperse the concentrated dispersion into additional matrix precursor material. Examples of suitable coatings for use with low-silicon aluminum alloys include metals, metal oxides, metal nitrides, metal carbides and metal borides. When a metal coating such as copper, molybdenum, nickel, zinc, tin, or titanium is used, it is preferably extremely thin, i.e. up to about 2 microns, to minimize any detrimental intermetallic interactions. Metal oxides useful herein include such as silica, alumina, chromia, nickel oxide, copper oxide, mullite, spinels, titania, magnesium silicate, lithium silicate, and the like. Metal nitrides useful herein include silicon nitride, titanium nitride, boron nitride, and aluminum nitride. Metal silicon compounds useful herein include molybdenum, copper and titanium silicides.

Silicon dioxide, which can be formed on silicon carbide by heating in air, is currently preferred, partially because it is particularly convenient to produce by merely heating silicon carbide powder at about 1300° C. for about 30 minutes. Alumina, which can conveniently be coated onto silicon carbide particles from a seeded sol to form the coating is also preferred.

Such coatings have generally not been found necessary for final composites prepared with magnesium-based alloys, because the formation of deletereous products has not been found to be as extensive, even if the magnesium is alloyed with aluminum.

The practice of the invention can be further appreciated from the following non-limiting examples in which all parts and percents are by weight unless otherwise specified.

Example 1

A quartz tube 16 cm in length and with an internal diameter of 2.2 cm was coated internally for a distance of about 15 cm with a suspension of colloidal graphite available from Acheson Colloids, Ltd., Brantford, Ontario, Canada, under the trade name AQUADAG. A supporting rod, narrower than the inside diameter of the quartz tube but having on one end a gas-permeable plug of porous refractory fireclay brick that fits tightly within the coated tube, was then inserted from the uncoated end and positioned so that the porous plug was about 10 cm from the opening of the coated end. The container thus formed by the coated tube end and the porous plug was filled with grit F600 green silicon carbide to a packing density of about 50 volume %, with the aid of a vibrating table contacting the container. (The size distribution of Grit F600 silicon carbide is described fully in publications of the Federation of European Producers of Abrasives, hereinafter "FEPA") The particular lot of Grit F600 used for this experiment was measured with a Coulter Counter and had 50% of its volume in particles with a size of more than 9.1 microns; 3% of the volume was made up of grits larger than 15.3 microns, 94% of the volume was made up of grits larger than 4.8 microns, and the central 75% of the volume was made up of grits with sizes between 6.2 and 12.2 microns. The central 75% of the volume is defined as the part of the sample excluding the largest and the smallest particles that each make up 12.5% of the total volume.

The top surface of the packed bed of SiC was covered with a layer of porous alumina paper (Product APA1 from Zircar Products, Florida, New York) and this end of the container was then wrapped with aluminum foil. The porous alumina paper is fitted tightly enough to keep the packed bed from falling out when the container is inverted and to serve as a filter to exclude oxides or other unwanted foreign matter when molten metal is later in filtrated into the packed bed. The aluminum foil allows the protected end of the container to be immersed in the molten aluminum alloy without contaminating the contents with a layer of oxide that forms spontaneously on molten aluminum alloys. Shortly after immersion, the aluminum foil melts. The amount of aluminum foil is too small to change the composition of the molten aluminum alloy to any significant extent.

The wrapped container with its packed bed was then placed in a gas tight desiccator that was evacuated to a pressure of no more than 0.01 bar and then backfilled with argon. The container as thus prepared was positioned within an apparatus illustrated in Figure 1. The quartz tube 1 now has the alumina paper 5 at the bottom of the packed bed 4, with the porous fireclay plug 3 and the support road 2 on top. The tube 1 is connected via a gas tight fitting 6 to a channel 7 that allows the input or exit of gas from the space above the porous plug independently of the space 8 in the upper part of the apparatus.

The tube with its packed bed was immersed as shown in Figure 1 in a bath of molten A357 aluminum alloy (which contains about 7% silicon) 9, with a melting point of 610°C, maintained within a graphite crucible 10 at a temperature of 700°C by a conventional heating element 11. The crucible and heater are within a gas tight space defined by container 12, which is protected from the heat of the heating element 11 by insulation 13. Space 8 was initially filled with argon gas at atmospheric pressure. After preheating the tube containing the packed bed for 5 minutes, at which point the thermocouple 15 showed that the temperature of the molten metal 9 had recovered to the desired value of 700°C. after being cooled by introduction of the packed bed and its container, the pressure within the furnace above the layer of molten alloy was increased at the rate of 1.36 bar/min by admission of additional argon gas through input channel 14. This pressure caused the fluid alloy to flow through the packed bed from the bottom, displacing gas from the top of the bed through the porous plug into the separate channel 7.

When the pressure reached 13.6 bars, the increase in pressure was discontinued and the pressure maintained at that level for five minutes. The entire furnace was then depressurized through outlet 15 and the tube containing the packed bed of SiC, now infiltrated with molten alloy, was removed and cooled in the air to produce a concentrated composite, which was separated from the quartz tube, by pushing from one end, and then cut into pieces with a diamond saw. A photomicrograph of a polished cross section of the concentrated composite produced is shown in Figure 2.

In a separate graphite crucible, 91 g of A357 alloy was melted and heated to 720°C, and a piece weighing 62 g of the concentrated composite prepared as described above was placed on top of the molten alloy. After ten minutes, the material was stirred with a graphite rod to effect a preliminary break-up of the concentrated composite, and a graphite rotating stirrer preheated to 600°C was then immersed and used to stir the melt for 5 minutes at 300 rpm. The crucible was then removed from the furnace and its contents poured into another crucible and cooled. The resulting composite according to this invention with 20 volume percent (hereinafter v/o) SiC was examined microscopically after preparing a polished cross section. There was good distribution of the SiC dispersates throughout the composite, with apparently intimate contact at most SiC-metal interfaces and little porosity, as shown in a micrograph of a cross section of the composite in Figure 3.

Example 2

Particles of grit F600 silicon carbide were put into the bottom of a steel crucible to give a packed bed with about 50 v/o SiC. A sufficient amount of molten alloy of 90% Mg - 10% Al to infiltrate the entire packed bed was poured over the bed, and the crucible with its contents placed inside a pressurizable furnace maintained at 700° C. Compressed argon was then admitted to the furnace until the pressure reached 34 bars. This was sufficient to cause the molten alloy to impregnate all of the packed bed except for a small pocket at the bottom into which the air originally present in the packed bed had been displaced.

A portion of the fully impregnated concentrated composite prepared as described immediately above was softened at 700° C. and mixed with an additonal amount of molten 90% Mg - 10% Al alloy chosen to result in a final composite with 20 v/o SiC. Mixing was initially accomplished with a hand-held stirring rod until the concentrated composite was sufficiently low in apparent viscosity to allow effective mechanical stirring. Mixing was then continued with a double helical stirrer operated at 400 revolutions per minute. This avoided entraining gas through vortex formation. After about five minutes stirring, a semi-solid slurry that could be cast into a mold resulted. The material was then cast and allowed to solidify. A well dispersed final composite was formed.

Example 3

This was performed in the same manner as Example 2, except that Grit F500 rather than grit F600 silicon carbide was used.

Example 4

This was performed in the same manner as Example 2, except that Grit F320 rather than grit F600 silicon carbide was used.

Example 5-7

The preparation of the concentrated composite for these examples was performed in substantially the same manner as in Example 2-4 respectively, except that (i) a slightly different apparatus, one that allowed evacuation as well as pressurization of the space within the container for the dispersates, was used; (ii) initially solid alloy material was added to the container above the packed bed; (iii) the space within the container for the dispersates was evacuated after the solid metal and dispersates had been placed within the furnace, which was maintained at 900° C, before pressurizing to cause infiltration; and (iv) a commercially pure magnesium alloy was used for the matrix.

The concentrated composite was mixed with additional molten matrix alloy in a special container, under an argon atmosphere, using an agitator similar to a turbine moving at 2,000 -3,000 revolutions per minute. A system of baffles in the container prevented any significant gas entrapment during mixing. The dispersion was mixed for about five minutes at a temperature of about 700° C. The stirrer was then immediately removed and the dispersion promptly cast in a copper chill mold about 9 mm deep. A well-dispersed composite with about 15 v/o dispersates resulted.

Example 8

This was performed in the same way as Examples 5-7 except that a finer particle size of silicon carbide, averaging 3 microns in size, was used.

Example 9

This example illustrates application of the invention to continuous casting and is accomplished with apparatus shown in cross section in Figure 4. Molten alloy 100 and concentrated composite are continuously fed into a chamber 102 maintained at a temperature that will keep the mixture at least partially fluid. From chamber 102 the mixture is pumped and blended by a rotor 103 into a mixing region 104, where it experiences vigorous agitation. The high shear rates in region 104 are achieved in a narrow gap 104 between chamber wall 105 sand a rotor 106. Both the chamber wall and the rotor have surfaces including a conic frustrum with the same taper angle, so that the gap width, and correspondingly the rate of shear, can be adjusted by relative vertical displacement between the rotor and the chamber wall. The well dispersed dispersion exits in region 107 and can be fed into a crucible for solidification processing, continuously cast into a billet, or the like.

Alternatively, the concentrated composite itself could be rotated vigorously in a bath of molten alloy so that portions of the concentrated composite are peeled off at the interface as the matrix of the concentrated composite softens under the influence of the higher temperature of the bath of molten alloy.

Example 10

This example illustrates another continuous method embodiment of the invention and may be understood with the aid of Figure 5, a cross sectional view of apparatus useful for the invention. A solid chamber 201 capable of withstanding the pressures involved is provided with conventional means for maintaining various temperatures in different regions in its interior and contains two inlets 202 and 203 and an outlet 204. At inlet 202, molten metal 205 is supplied under pressure. At inlet 203, dispersates 206 are supplied at an appropriate rate and also under pressure by means of a ram, screw feeder, or other appropriate device known to those skilled in the art.

During operation of the continuous process of this invention, chamber 201 is kept at a temperature that will maintain molten metal in regions 205 and 207 and at a temperature too low to melt the metal used at the top of region 206, which constitutes a packed bed of dispersates. The flow of dispersates from zone 203 is maintained in a downward direction by mechanical pressure exerted against the packed bed of dispersates, but this does not prevent metal from filling the interparticle space in the packed bed of dispersates in the lower part of the entry region for dispersates, where the temperature is sufficiently high to keep the metal molten. Thus a zone of concentrated composite according to this invention forms in region 207, but upward penetration of the metal is limited by its solidification in the upper part of the inlet 203, creating a more or less distinct boundary between region 207 containing concentrated composite and region 206 with dispersates and gas only.

In the region where the molten metal 205 contacts the concentrated composite 207, the flow rate of the metal is accelerated by a constriction caused by a bulge 208 in the chamber wall. In the region between 208 and 207, the concentrated composite is continuously entrained downstream by the rapidly flowing molten metal and it is sheared and dispersed into the flowing metal. At a sufficient distance downstream from the constriction, a region 209 of substantially homogeneous and nonporous dispersion is obtained. This dispersion can be continuously cast from the outlet 204 to yield a solid continous billet 210 of the finally desired composite. The volume fractions of metal matrix and dispersates are controlled by regulating the relative feeding rates of dispersates and molten metal at their inlets 203 and 202 respectively.

Instead of a constriction, separate mechanical or electromagnetic stirring could be used to disperse the concentrated composite into additional matrix precursor.

Example 11

This was performed in the same manner as Example 1, except that the SiC particulates used were a mixture of equal volumes of FEPA Grit F400, Grit F500, and Grit F600. The Grit F600 had the same size distribution as in Example 1. The Grit F500 material had 3% of its volume in particles larger than 22.5 microns, 50% of its volume in particles larger than 13.7 microns, 94% of its volume in particles larger than 8.7 microns, and the central 75% of its volume in particles with sizes between 10.6 and 17.7 microns, all as measured by a Coulter Counter. Using the same measurement technique, the Grit F400, material had 3% of its volume in particles larger than 25 microns, 50% of its volume in particles larger than 17 microns, 94% of its volume in particles larger than 12 microns, and the central 75% of its volume in particles with sizes between 13 and 20. 5 microns.

The central 75% of the volume of the mixture had particles between 7.8 and 19 microns, 3% of the volume of the mixture was in particles smaller than 5.2 microns, and 94% of the volume of the mixture was in particles larger than 21 microns. The final composite produced had an apparently uniform distribution of all particle sizes of SiC within the matrix when examined in cross section.

Example 12

This was the same as Example 1, except that the dispersates used were boron carbide rather than silicon carbide. Good redistribution of the concentrated composite was obtained in the final composite.

Example 13

This was performed in the same as Example 1, except that (i) 100 g of concentrated composite and 215 g of additional A357 alloy were used, to give a 15 v/o composite; (ii) the melt temperature during the mixing of the concentrated composite into the additional molten alloy was only 670° C rather than 700° C; and final stirring was for only 2.5 minutes instead of five. The difference in temperature considerably increased the apparent viscosity during the mixing of the concentrated composite with additional matrix material, and some large air pores were introduced during the stirring and preserved in the final composite. Therefore, even though the SiC dispersates were again well dispersed within the final composite, the results were less preferable than for Example 1.

Example 14

This was performed in the same way as Example 1, except that (i) the alloy used was Type 6061 alloy rather than the A357 and (ii) 100 g of concentrated composite and 149 g of additonal molten alloy were used in the final mixing step.

Type 6061 alloy contains 0.6% Si, 1.0% Mg, 0.3% Mn, and 0.2% Cr, with the balance aluminum. Presumably because of the very low silicon content, the dispersion of the concentrated composite within the final composite was not nearly so good as in Example 1. A micrograph of a cross section of the final composite produced in this example is shown in Figure 6.

Example 15

This was performed in the same way as Example 14, except that the alloy used was 10% Si - 90% Al. The result contrasted sharply with that of Example 14, in that the distribution of the SiC dispersates within the final composite was very uniform.

Example 16

This was performed in the same way as Example 14, except that the alloy used contained 99.9% aluminum. The dispersion of silicon carbide in the final composite was less uniform than that achieved in Example 14.

Example 17

This was performed in the same way as Example 16, except that (i) the temperature both for preparation and for mixing of the concentrated composite was raised to 800° C; and (ii) 71 g of concentrated composite and 152 g of additional alloy were used in the mixing step, which should have given a final composite with only 15 v/o SiC. In fact, however, mixing the concentrated composite with additional metal proved to be practically impossible. X-ray diffraction of a sample of the concentrated composite showed the presence of aluminum carbide at the interfaces between the dispersates and the matrix. This is believed to be the reason that the concentrated composite was so difficult to break up.

Example 18

This was performed in the same manner as Example 17, except that (i) the final mixing was at 720° C rather than 800° C and (ii) the SiC particulates used were heated in air at 1300° C for thirty minutes before being infiltrated to form the concentrated composite. This treatment is known to form a layer of SiO_2 on the surface of silicon carbide. The silica surface greatly retards the formation of aluminum carbide, as confirmed by an X-ray analysis of this concentrated composite, and thus the concentrated composite could easily be dispersed in the final mixing step. A micrograph of a cross section of the final composite thereby produced is shown in Figure 6.

Example 19

This was the same as Example 1, except that the SiC particulates, before forming the concentrated composite, were coated with alumina in the following manner: a boehmite sol at 10 w/o total solids containing 0.15 w/o of fine alpha alumina seeds, prepared in a state of incipient gellation as described in detail in U.S. Patent 4,623,364 was prepared. One liter of this sol was mixed with one kilogram of FEPA Grit 600 SiC, and the mixture then pumped through a NIRO spray drier, which caused the SiC to be coated with an apparently uniform coating of dried alumina gel when examined by as scanning electron microscope. The coated particulate was then heated at 1200° C for thirty minutes to convert the alumina gel to alpha alumina. Conversion was confirmed by x-ray diffraction analysis that showed alpha SiC and alpha alumina as the only phases present.

The final composite prepared in this Example showed an excellent uniformity of dispersion of the SiC within the matrix.

Comparative Example A

SiC was coated with Cr metal by an evaporation-condensation process to 29%. Infiltration attempts with both A357 and Al· 99.9 were made using quartz tubes 20 cm. long and .5 cm. ID. The temperature of the infiltrating aluminum was varied between 700° C and 800° C, and the pressure varied up to 400 psi. In both cases infiltration was negligible. It is believed that the chrome metal was dissolved by the molten aluminum producing an aluminum chrome alloy. Small additions of chrome to aluminum significantly raise the melting temperature, thus freezing the metal front before infiltration can occur. Thus chrome metal is not a useful coating material.

Comparative Example B

SiC powder, coated as in Comparative Example A, was calcined in air at 1200° C for 1/2 hour to promote the formation of chromia around each particle. The calcining only converted the surface of the chrome coating to chromia. This powder was packed and infiltrated with A357 as in Example 1 using a pressure of 375 psi and a temperature of 750° C. 89 g of this master composite was heated to 850° C with 209g of A357 to give a final composition of 14 %. After 2 1/2 hours, the master composite pieces had not yet broken up; thus little dispersion occured. The protective barrier of Cr_2O_3 on each particle dissolved, allowing the Al to react with the chrome, as in Comparative Example A, to form a high melting alloy and to prevent the dispersion of the master composite. Thus a surface chromia layer on a predominantly chrome coating was not suitable.

Example 20

A master alloy was prepared using A357 and SiC coated with chrome to 3.5 wt% and calcined as in Comparative Example B. In this case, however, the Cr was completely oxidized to chromia. The infiltration occured at 750° C with 400 psi. 94.9 g of this concentrated dispersion sample was dispersed into 235 g of A357 to give a composite of 13.4 wt% SiC. This took 15 minutes at 850° C. Micrographs indicate a good dispersion with a few clumps of master alloy remaining which can be broken down with improved stirring. In this case the chrome oxide coating prevented any reaction between the aluminum metal and the SiC to allow dispersion of the master alloy to occur. The absence of any chrome metal in the coating also prevents the melting point of the alloy from rising which had ben found to prevent dispersions of the master composite in Comparative Examples A and B.

Example 21

A coating of Si_3N_4 on SiC particulate was produced by heating SiC in flowing nitrogen gas to 1425° C. A master composite was produced as in Example #1 using A357 at 300 psi and 725° C. 75 g of this master composite was stirred into 192 g of A357 as in Example 20 to give a final fraction of 13.1% SiC. Dispersion occured easily. Micrographs of the final composite indicate good dispersion of the coated SiC particulate without any noticeable reaction products being formed between the metal matrix and the coated SiC dispersates.

Comparative Example C

SiC was coated to 8.3% Ni metal using a NiB electroless plating solution. Infiltration was accomplished using quartz tubes, as in Example #19, with the A357 at 725° C and applying a pressure of 200 psi. 9.3 g of this master alloy was dispersed into 57.9 g of A357 using a small porcelain crucible and a graphite stirring rod. Furnace temperature was set to 800° C. The master composite did not disperse evenly, presumably due to nickel-silicon alloy formation, thus indicating that a nickel metal coating is not suitable with this aluminum alloy.

Example 22

The procedure of Comparative Example C was repeated reducing the nickel content on the dispersates to 2% and using Al 99.9 as the matrix material and in both the infiltration and the dispersion. A good dispersion results.

Example 23

SiC was given a total 9.5 % coating of a chromia-alumina solid solution. This coating was produced by mixing equal weights of SiC and a 30 % solids solgel of $Cr(NO_3)_3 \cdot 9H_2O$ and $Al_2O_3 \cdot H_2O$. The resulting slurry was dried to a powder and fired at 1250° C to remove structurel water in the coating materials and to convert the nitrate to an oxide. This SiC was infiltrated with A357 as in Example 1 using a temperature of 725° C. and a pressure of 160 psi. 5.8 g of this master alloy was then stirred into 60.7 g of A357 to give a composite having 4.0% SiC. Dispersion was good.

Example 24

A 6% molbdenum coating was placed on silicon carbide particles by mixing coarse molybdenum powder with F600 SiC in an appropriate weight ration and heating in a vacuum furnace to evaporate the molybdenum and redeposit it on the SiC particles. The coated particles were then processed as in Example 1 with A357 alloy to form a concentrated dispersion thereof containing 54% dispersates. The concentrated dispersion was then stirred into further A357. Good break-up of the concentrated dispersion is observed and a uniform final composite is produced.

Example 25

The procedure of Example 24 was repeated to produce a 6% titanium metal coating on silicon carbide dispersates, to use those dispersates to prepare a concentrated dispersion, and to use the concentrated dispersion to prepare a final uniform dispersion. A good dispersion resulted.

Example 26

The procedure of Example 25 was repeated to produce the titanium metal coated silicon carbide dispersates and then the titanium coating was oxidized to converted it to titania. Infiltration with A357 at a pressure of 160 psi was barely adequate to produce a void-free concentrated dispersion, but when repeated at 300 psi the process proceeded smoothly. Good final dispersions were produced in each case.

Example 27

A titanium nitride coating was placed on silicon carbide dispersates by (i) forming a silica and carbon diffusion layer by calcining the SiC in air at 1100° C., (ii) coating titanium metal thereon by a pack diffusion process, and then (iii) nitriding at 925 - 1025° C. to convert the metallic Ti to TiN. The resulting dispersates were readily infiltrated with pure aluminum to form a concentrated dispersion which was stirred into further pure aluminum to produce a well- dispersed final composite product.

Claims

1. A process for the manufacture of a composite of a plurality of discrete solid dispersates within a solid matrix material, which comprises

(a) forming a concentrated dispersion of said dispersates within a first quantity of a fluid material that is a precursor of a portion of said solid matrix;

(b) mixing at least a portion of said concentrated dispersion with a second quantity of a fluid material which is a precursor of the matrix of the final composite;

(c) dispersing the dispersates contained in said at least portion of said concentrated dispersion into the resulting fluid material; and

(d) solidifying said fluid material from step (c) to form the final composite.

2. A process according to claim 1, wherein a packed porous bed of said plurality of dispersates is formed and said packed porous bed of dispersates is infiltrated with said first quantity of fluid material.

3. A process according to claim 2, wherein said packed porous bed is evacuated before said infiltrating.

4. A process according to any one of the preceding claims, which comprises solidifying at least part of the matrix of said concentrated dispersion before step (b) is performed.

5. A process according to any one of the preceding claims, wherein said dispersates are comprised predominantly of silicon carbide, boron carbide, silicon nitride, or aluminum nitride.

6. A process according to any one of the preceding claims, wherein said dispersates have a surface layer of a barrier material which retards, at the temperature of formation of the concentrated dispersion and at the temperature of formation of the final composite, a chemical reaction that would otherwise occur between the material of the dispersates and said fluid material.

7. A process according to claim 6, wherein said barrier layer is comprised predominantly of a metal, a metal oxide, a metal nitride, a metal silicide, a metal carbide, or a metal boride.

8. A process according to claim 6 or 7, wherein the first quantity of fluid material contains a material which facilitates wetting of the dispersates without promoting deleterious chemical reactions.

9. A process according to any one of claims 6-8, wherein said barrier material comprises silicon dioxide.

10. A process according to any one of the preceding claims, wherein the mixing of at least a portion of the concentrated composite with the second quantity of fluid material is performed at a temperature at least 70° C. higher than the melting point of the matrix of the final composite.

11. A process according to any one of the preceding claims, wherein the concentrated dispersion comprises 25 to 85 weight percent dispersates and 75 to 15 weight percent matrix precursor.

12. A composite comprising:

(a) a matrix

(b) from 5 to 40 v/o of discrete dispersates; and

(c) not more than 5% pores, voids, and/or gases.

13. A composite according to claim 12, wherein the matrix is aluminum, an aluminum alloy, bronze, copper, a copper alloy, magnesium, a magnesium alloy, titanium, a titanium alloy, zinc, or a zinc alloy.

14. A composite according to claim 13 or 14, wherein the dispersates are of silicon carbide, silicon nitride, aluminum nitride, alumina, titania, silica, boron carbide, a boride, a carbide, a silicide, or diamond.

15. A composite according to claim 13 or 14, wherein the dispersates have a surface layer of a barrier material which retards a chemical reaction that would otherwise occur between the material at the core of the dispersates and said matrix material.

16. A composite according to claim 15, wherein said barrier layer is comprised predominantly of a metal, a metal oxide, a metal nitride, a metal silicide, a metal carbide, or a metal boride.

17. A composite according to claim 15 or 16, wherein said dispersates are predominantly silicon carbide and the matrix is predominantly comprised of aluminum containing less than 12% silicon.

FIG. 1

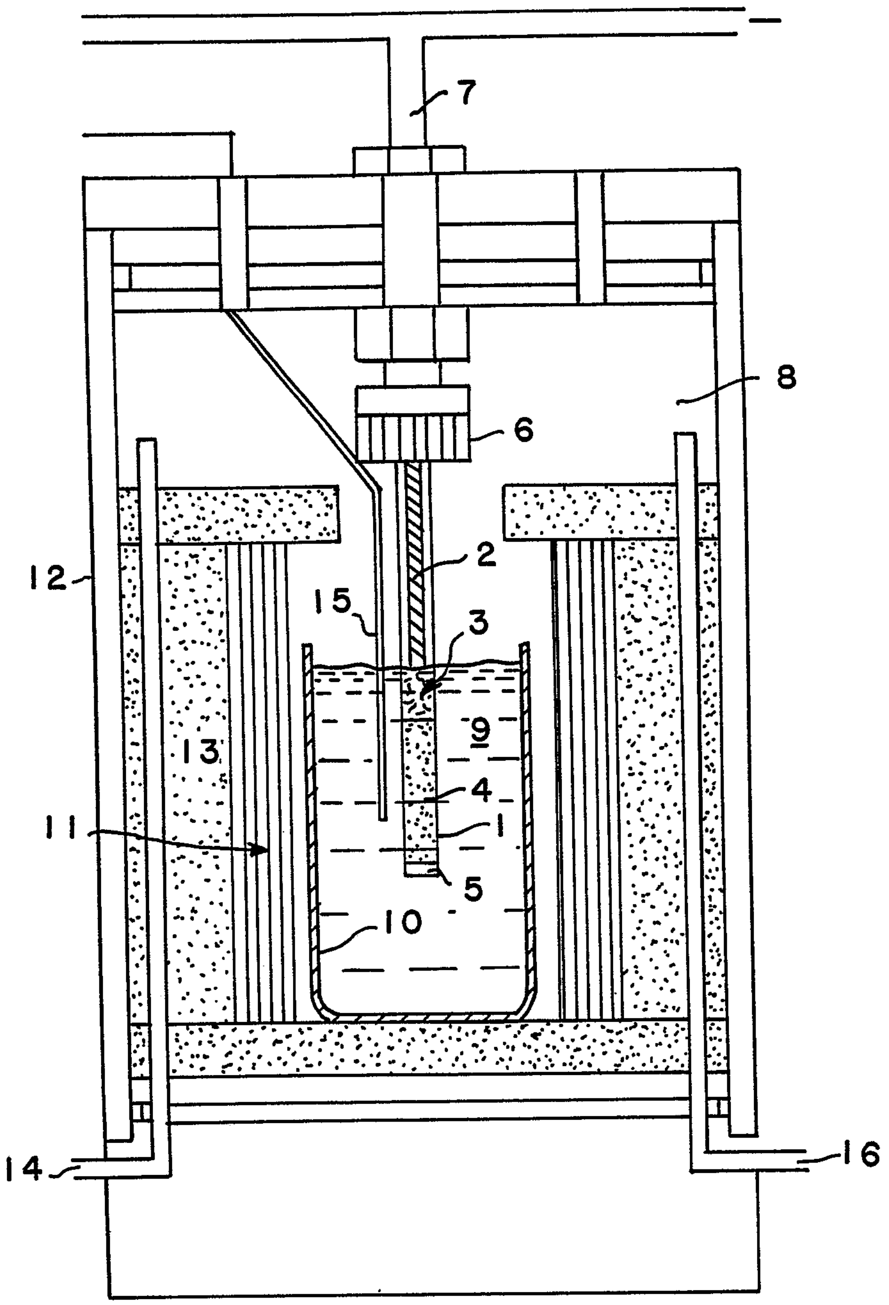
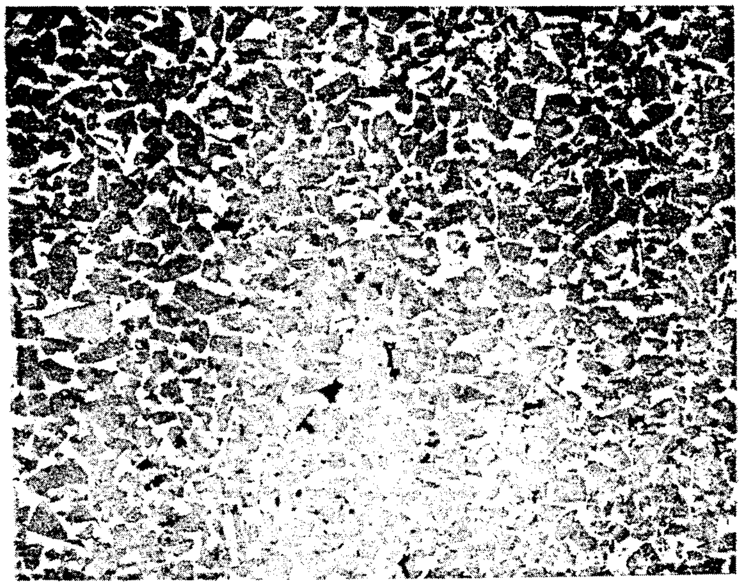
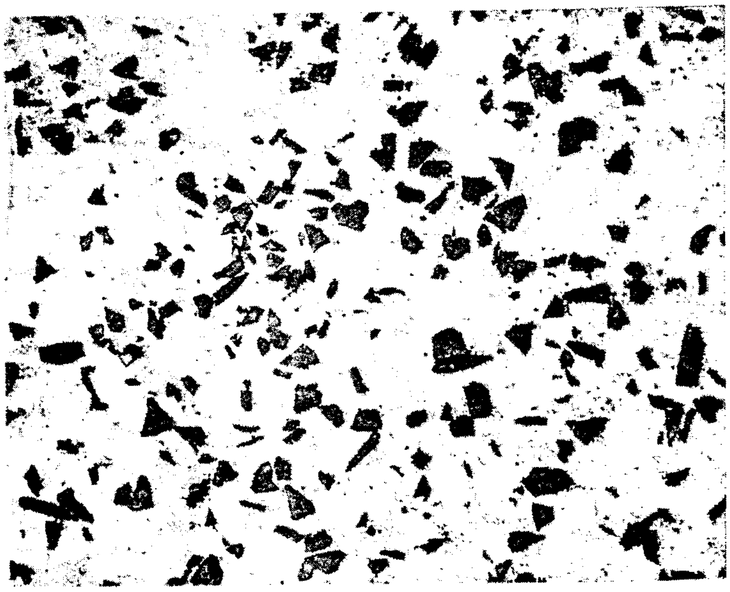


FIG. 2



A357/SiC F600 M.A.
400X 3/21/88

FIG. 3



A357/F600 20% FROM M.A.
400X 3/22/88

FIG. 4

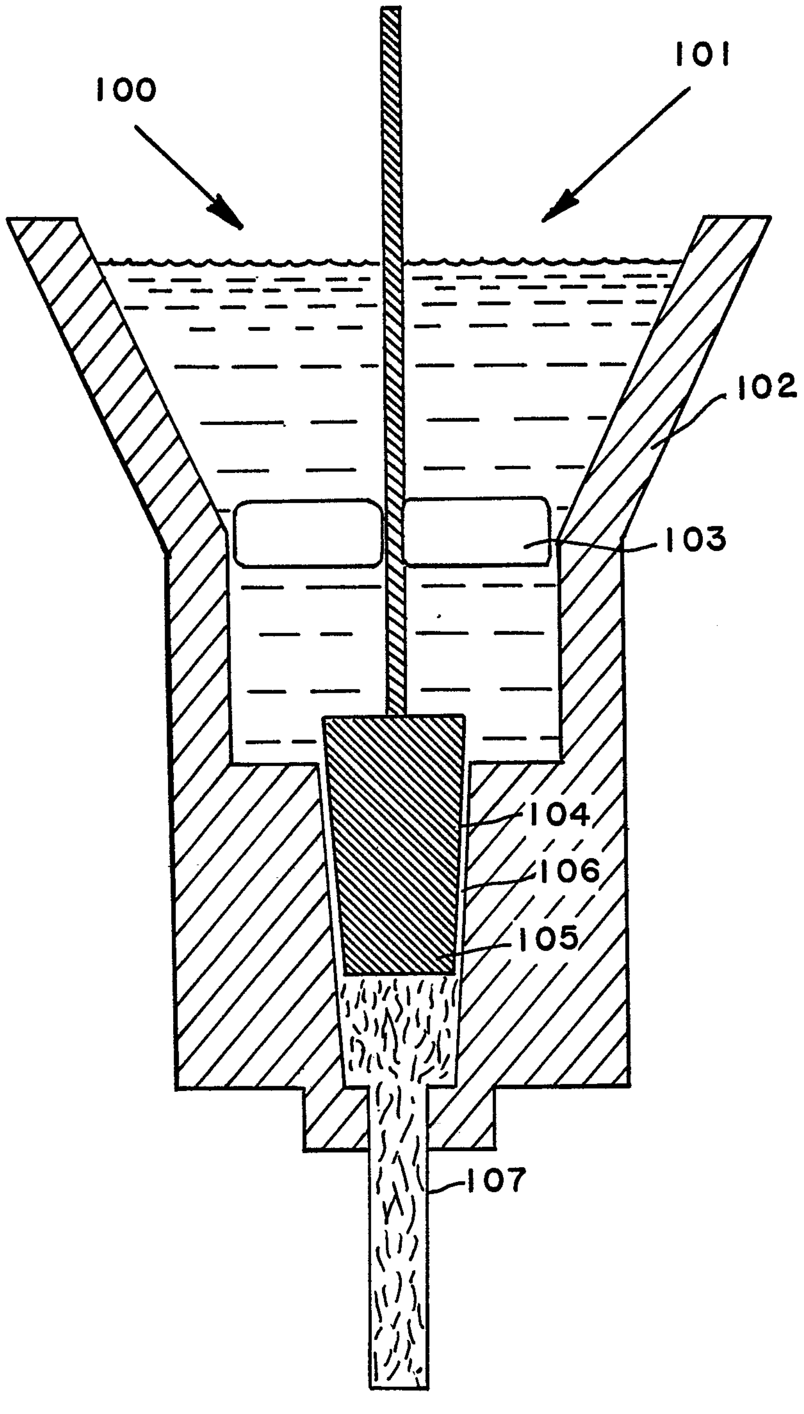


FIG. 5

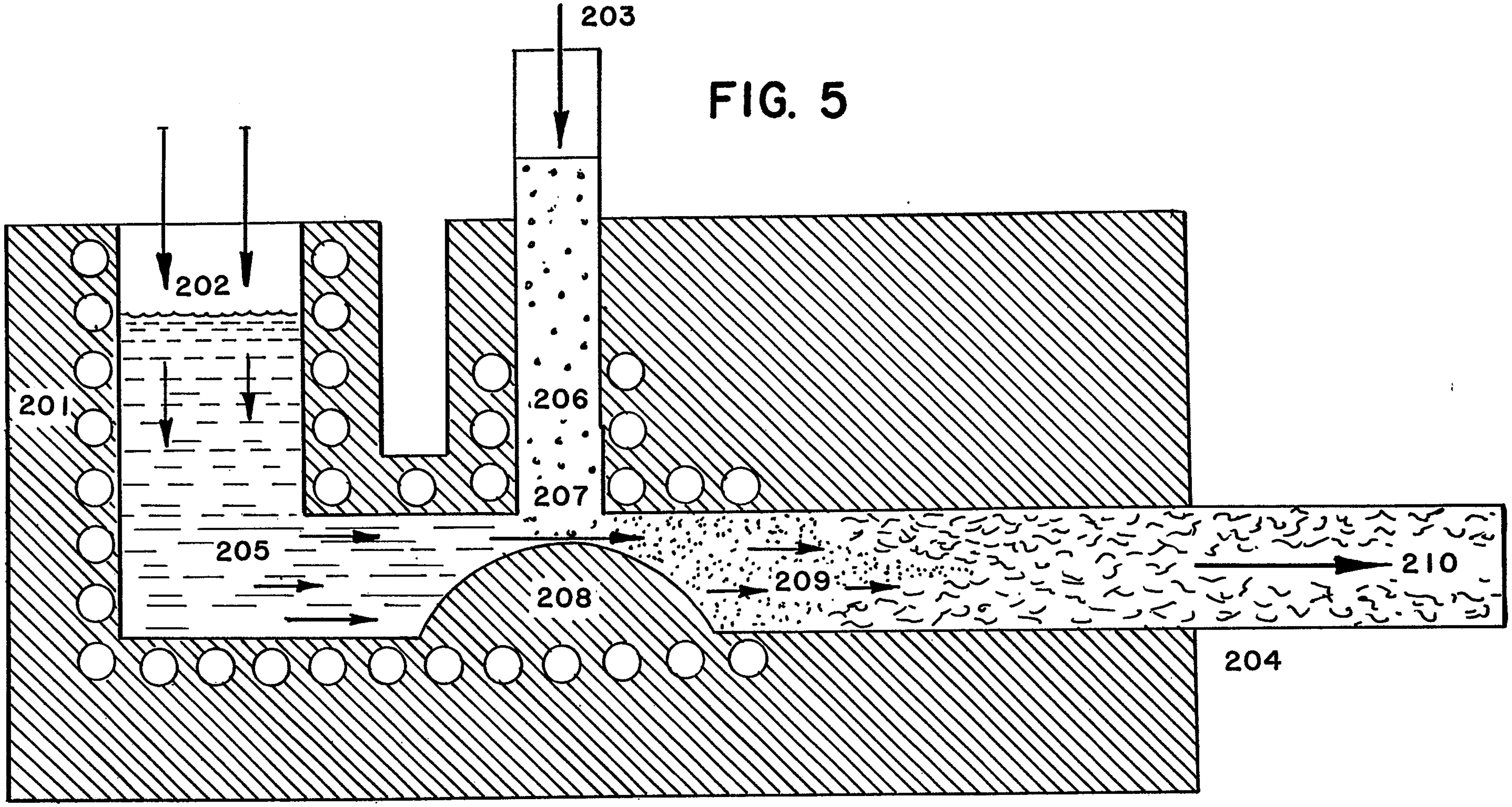
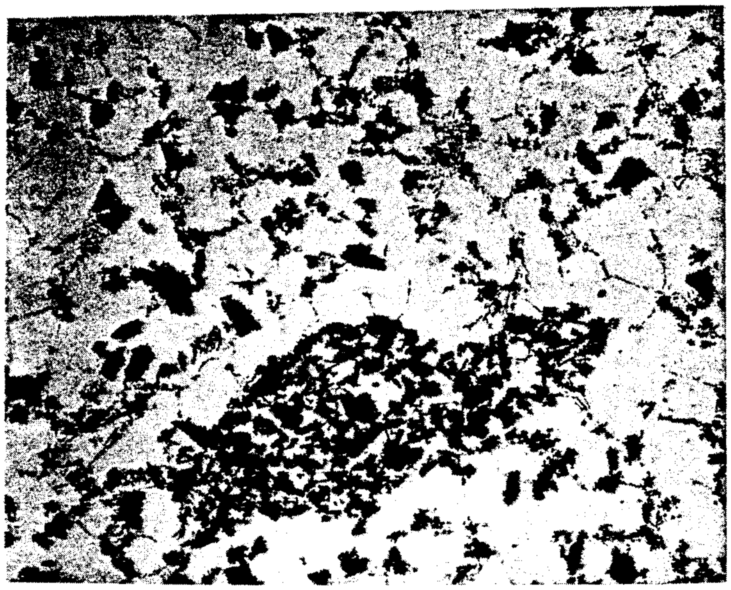
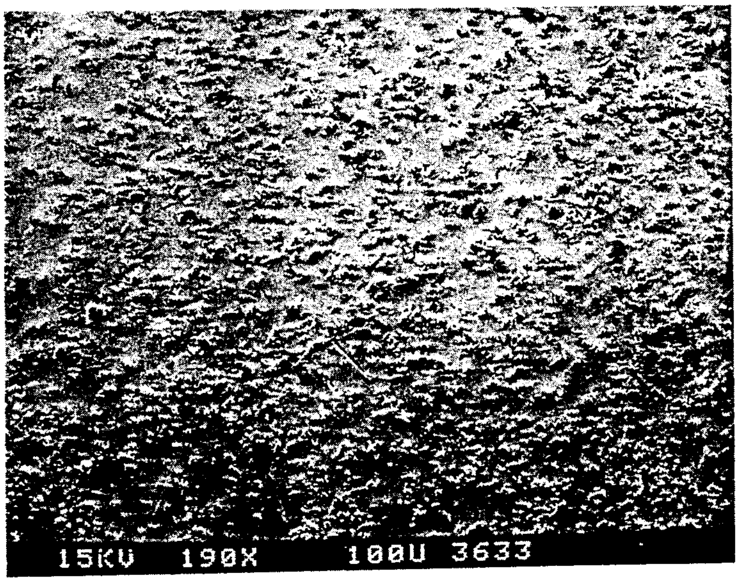


FIG. 6



6061/SiC F600 20% FROM M.A.
400X 3/21/88

FIG. 7



MICROSTRUCTURE OF 99.9Al/15VOL%
SiC COMPOSITE
SiC HEAT TREATED IN AIR 1300C
30 MIN. BEFORE INFILTRATION

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 11 0482

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	EP-A-0 104 682 (THE DOW CHEMICAL CO.) * Page 4, lines 21-26; page 5, lines 3-28; page 7, example 1; claim 2 *	1,4,5,10-14	C 22 C 1/10
Y		2,3,6-8,15,16	
Y,D	EP-A-0 256 600 (NUOVA SANIM S.p.A.) * Page 2, column 2, lines 12-27 *	2	
A,D		6,15	
Y	EP-A-0 150 519 (NEDERLANDSE CENTRALE ORGANISATIE VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK ONDERZOEK) * Abstract *	2,3	
Y	US-A-4 741 973 (CONDIT et al.) * Column 2, lines 1-34 *	6,7,15,16	
Y	US-A-2 793 949 (IMICH) * Column 1, lines 44-47; column 2, lines 22-29 *	8	
A,D	JOURNAL OF METALS, February 1988, pages 12-19, New York, US; A. MORTENSEN et al.: "Solidification processing of metal-matrix composites"		
A,D	JOURNAL OF MATERIALS SCIENCE, vol. 13, no. 1, January 1978, pages 329-335, Chapman and Hall Ltd; B.C. PAI et al.: "Production of cast aluminium-graphite particle composites using a pellet method"		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 22 C
B 22 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19-09-1989	ASHLEY G.W.

CATEGORY OF CITED DOCUMENTS

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