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(54) Titre : FABRICATION D'ALLIAGES CONTENANT DES PARTICULES FINES DISPERSEES
(54) Title: MANUFACTURE OF ALLOYS CONTAINING DISPERSED FINE PARTICULATE MATERIAL

(57) Abrégé/Abstract:
A method of preparing a metal alloy comprising a dispersion of particles of a first metallic material consisting of one or more refractory hard metals in a matrix of a second metallic material includes establishing a molten body of the second metallic material and introducing solid particles of the first metallic material into the molten body. Alternatively solid particles of a metalloid which reacts with the second metallic material to form particles of the first metallic material may be introduced into the molten body. The first metallic material has a higher melting point than the second metallic material and is substantially insoluble therein. The molten body is then stirred at a rate sufficient to effect shearing of the surfaces of the particles such that the surfaces are wetted by the molten body, and the molten body containing the resultant dispersion is cast in any desired manner.

ABSTRACT OF THE DISCLOSURE

A method of preparing a metal alloy comprising a dispersion of particles of a first metallic material consisting of one or more refractory hard metals in a matrix of a second metallic material includes establishing a molten body of the second metallic material and introducing solid particles of the first metallic material into the molten body. Alternatively solid particles of a metalloid which reacts with the second metallic material to form particles of the first metallic material may be introduced into the molten body. The first metallic material has a higher melting point than the second metallic material and is substantially insoluble therein. The molten body is then stirred at a rate sufficient to effect shearing of the surfaces of the particles such that the surfaces are wetted by the molten body, and the molten body containing the resultant dispersion is cast in any desired manner.

PATENT APPLICATION

MANUFACTURE OF ALLOYS CONTAINING DISPERSED FINE PARTICULATE MATERIAL

The present application is directed to a novel method of preparing metal alloys containing finely divided particulate metal or intermetallic compounds as a substantially insoluble second phase. A particular embodiment is directed to manufacture of aluminum base master alloys containing titanium together with boron or boron alone.

BACKGROUND TO THE INVENTION

Products containing dispersions of fine particulate non-metallic material in metals and alloys, commonly known as metal matrix composites, are well known in metallurgical engineering. Examples are dispersions of metal oxides, nitrides, carbides and the like in a matrix of aluminum or alloys thereof. Commercial use of such composites was delayed for many years by the need to develop consistent and reliable means of manufacture of sound defect-free components. Mass production of such components required melting and casting methods for conventional metal alloys to be adapted to metal matrix composites. This required complete wetting of the particle surfaces by the molten matrix metal which, in the early stages of this technology, was difficult to achieve.

A number of different methods of achieving such wetting have been proposed. An early proposal by the International Nickel Company was to coat the particulate with metallic nickel by exposure to gaseous nickel carbonyl at an appropriate temperature. Metallic zinc and lithium and magnesium oxide have also been proposed as coating materials.

A more successful approach has been the use of high shear stirring of molten metal containing solid non-metallic particulate using specially designed power-driven rotor systems to develop high relative velocity between particulate dispersate and molten metal. Such methods have been disclosed by Klier et al in U.S patent 4,961,3461 and Skibo et al in U.S patent 4,786,467. Klier et al disclose an upright tapered cylindrical vessel containing a centrally located high speed rotor into which the molten matrix metal containing the particulate dispersate is introduced. The rotor shaft extends below said rotor to the bottom of the vessel in which a second rotor is positioned. The second rotor is conical in shape and positioned inside a fixed tapered wall. The narrow gap between the wall and the rotor serves as a zone of high shear and can be varied at will by raising and lowering the rotor. Skibo et al disclose a circular section vessel into which a body of the molten matrix metal is introduced and into which the required particulate dispersate is subsequently fed. The vessel contains a specially designed centrally located dispersing impeller to effect high shear stirring. This is optionally augmented by a sweeping impeller located at the periphery of the vessel to sweep the particulate to within the orbit of the dispersing impeller. This operation is carried out under selected temperature and time conditions to promote wetting by the molten metal of the exposed particulate surfaces.

A conventional method for manufacturing metal alloys with which the present invention concerned is to establish a stirred body of the molten metal into which is introduced a chemical compound of halides or double halides of the desired metallic additive(s) in powder form. Stirring is typically effected by electric induction. The compound reacts with the molten metal to form the desired metallic additive which on solidification and casting is present in particulate form within the cast product matrix. Examples of metal alloys of the present invention are aluminum base master alloys containing titanium and boron. These are widely used in aluminum and aluminum alloy manufacture by addition to molten metal prior to casting to effect refinement of the as-cast grain size. The titanium and boron in such master alloys are typically present as insoluble particles of titanium diboride, TiBsub2, suspended in the melt whilst titanium in excess of the stoichiometric proportions for formation of TiBsub2 (2.2:1) is in solution in the molten metal. Such titanium precipitates as the aluminide, TiAlsub3, on cooling and solidification. A typical and commonly used formulation for such a master alloy is aluminum 94%-titanium 5%- boron 1%.

A conventional method for manufacture of such master alloys is by addition to a stirred body of unalloyed aluminum of a mixture of potassium titanium fluoride, Ksub2AlFsub6 and potassium borofluoride, KBFsub4 as powders premixed in the appropriate proportions to obtain the desired master alloy formulation. Optionally, a portion of the titanium in excess of the aforesaid stoichiometric requirements can be added as solid unalloyed titanium metal or as an aluminum titanium master alloy (e.g. containing 20 % titanium). Such additions are made after completion of the mixed powder addition. The entire process is typically carried out in a low or medium frequency electric induction furnace, the electric power providing both heat and continuous stirring. Such stirring is essential not only to effect uniform dispersion of the alloying ingredients but also to minimise gravity segregation of the titanium diboride particles within the melt. The final stage of the process is casting the master alloy in an appropriate form for the desired final product, e.g. an ingot for remelting or further working directly to rod on a continuous casting machine.

It is desirable that casting take place as soon as possible after the alloying process to minimise both gravity segregation and agglomeration of the titanium diboride particles. The particles serve to effect grain refinement when the master alloy is introduced into molten aluminum or alloys thereof. For this to be efficiently carried out, it is essential that the size of the titanium diboride particles in the master alloy be strictly controlled within given limits. For instance, a master alloy user may require the particle size to be within the range of 1/4 to 3 microns. Moreover, any coarse particles or agglomerates may function as hard inclusions and impair the mechanical properties of the final product.

Aluminum-base master alloys containing boron alone are widely used in the aluminum industry for aluminum conductor alloys requiring high electrical conductivity. Such conductivity may be impaired by small quantities of the transition metals, titanium, chromium and vanadium commonly present in solution in commercial aluminum, rendering the product unsuitable for its intended use. Boron will combine with the aforesaid impurities to precipitate them as the borides thereof, in which form they have little or no effect on conductivity.

In the conventional manufacturing process of the master alloy, boron is introduced to molten aluminum in the form of potassium borofluoride powder in a process analagous to that described above for aluminum titanium boron master alloy manufacture. Boron combines with the aluminum to form the diboride, AlBsub2, or the dodecaboride, AlBsub12, depending on boron content and production conditions. Commercial master alloys typically contain either 3 or 4% boron. Particle size requirements are less stringent than for Al-Ti-B alloys. However, the borides must be fine enough to react completely with the transition metals during the production time period available between addition of the master alloy and casting of treated product. This can be particularly critical when the master alloy is fed in rod form to the casting trough of the treated product.

The above-described manufacturing methods for both Al-Ti-B and Al-B master alloys suffer many serious disadvantages. Firstly, use of the double fluorides of both titanium and boron entail severe environmental problems. The reaction with molten aluminum generates volatile fluorine-containing gases which must be contained and disposed of. This requires elaborate emission control installations which are expensive to install and maintain and liable to malfunction. The reaction products captured by the installation must also be disposed of in an environmentally acceptable manner. Volumes of molten fluoride-containing slags are also generated. Whilst these may have a commercial value, elaborate equipment is required for their separation from the molten alloy product and in either disposal or processing and packaging. These processes increase labour requirements.

Particle size control, particularly in Al-Ti-B master alloy production requires close control of temperature and time conditions, not always successfully achieved in an industrial environment. Stringent microscopic examination may be required before packaging and shipment to ensure compliance with the user's specification.

SUMMARY OF THE INVENTION

The present invention is based on the realisation that the various methods and apparatus for high shear stirring originally developed and used for manufacture of metal matrix composites can also advantageously be applied to manufacture of certain types of metal alloys. The invention provides a method of preparing a dispersion of particles of a first metallic material comprising one or more refractory hard metals in a matrix of a second metallic material which comprises the metal or alloy matrix. The term "refractory hard metals" as used herein is based on the characterisation provided in Schwarzkopf, Paul et al, Refractory Hard Metals, New York, Macmillan, 1953, Chapter I and includes carbides, nitrides, borides and silicides of the transition elements of the fourth to sixth groups of the periodic table. The present invention also applies to borides of aluminum. According to one aspect of the invention, a molten body of the second metallic material is established into which solid particles of the first metallic material are introduced. During this step, the molten body is stirred at a rate sufficient to establish relative shearing of the particle surfaces such that they become wetted by the molten metal. The resultant alloy is then cast by any desired method. The particulate first metallic material must have a higher melting point than the second metallic material and be substantially insoluble therein.

According to another aspect of the invention, a molten body of the second metallic material is established into which are introduced solid particles of a metalloid which chemically reacts with the second metallic material to form particles of said first metallic material. The term "metalloid" is used here as defined in the McGraw-Hill Encyclopedia of Science and Technology, 8th Edition, Volume 11, 1997, page 67, namely an element which exhibits the external characteristics of a metal but behaves chemically both as a metal and a non-metal. During this process, the molten body is stirred at a rate sufficient to establish shearing of the metalloid particle surfaces such that they become wetted by the molten metal thereby facilitating the reaction. The resultant alloy is then cast by any desired method The particulate first metallic material must have a higher melting point than the second metallic material and be substantially insoluble therein..

In both the above aspects of the invention, it is preferred that the molten body be established in an upright cylindrical vessel heated by any desired means. Where fuel-fired heating is used, however, the combustion products are preferably excluded from contact with the molten metal to avoid contamination or gas pick-up. Stirring of the molten metal body may be effected by a one or more power driven rotating impellers which serve to distribute the added particulate material and to effect shearing of the particulate surfaces and wetting thereof by the molten metal.

One embodiment of the present invention is directed to the manufacture of aluminum-base master alloys containing titanium and boron in which the boron is combined as the intermetallic compound TiBsub2. The method comprises establishing a molten body of unalloyed aluminum, into which particulate titanium diboride is introduced whilst effecting high speed stirring of said body. Shearing action of the molten aluminum on the titanium diboride particle surfaces is thereby effected which, as a result, become wetted by the aluminum. Titanium in excess of the stoichiometric requirements for TiBsub2 formation is also added in metallic form, but there is no requirement for this to be as powder. Such titanium, for example, may be added as solid ingot or the like or as an aluminum-titanium master alloy.

Another embodiment of the invention is directed to the manufacture of aluminum-base master alloys containing boron present as one or both borides of aluminum, AlBsub2 and AlBsub12. In one aspect of this embodiment, a molten body of unalloyed aluminum is established into which particulate aluminum boride is introduced in the same way as titanium diboride as heretofore. In yet a further aspect, elemental boron is introduced. Boron is classified as a metalloid in the McGraw-Hill Encyclopedia of Science and Technology, 8^{th}. Edition, Volume 3, 1997, page 11. The molten body is stirred a using a high speed rotor to effect shearing and wetting of the boron particle surfaces. A chemical reaction of the boron with the aluminum is thereby promoted to form one or both borides of aluminum.

Both titanium diboride and elemental boron are available on the market in particulate form. Whilst most commercial material is micron sized, sub-micron materaial is also available. The previously mentioned disadvantages of the conventional methods of manufacture are substantially overcome by the present invention. Pollution problems associated with use of fluoride materials are eliminated resulting in major cost savings in emission control equipment. Particle size of the metallic alloying materials can be more closely controlled and finer average second phase particle sizes are feasible. No major quantities of slag are generated other than the dross normally generated by melting aluminum. In preferred embodiments of the invention, the foregoing processes can be operated either under vacuum or controlled inert gas atmosphere such as argon. These measures significantly improve alloy cleanliness.

The advantages of the invention and further embodiments thereof will now be readily apparent to a person skilled in the art, the scope of the invention being defined in the appended claims..

CLAIMS

1. A method of preparing a metal alloy comprising a dispersion of particles of a first metallic material consisting of one or more refractory hard metals in a matrix of a second metallic material comprising the steps of:-

(i) establishing a molten body of said second metallic material

(ii) introducing solid particles of said first metallic material into said molten body, whilst

(iii) stirring said molten body at a rate sufficient to effect shearing of the surfaces of said particles such that said surfaces are wetted by said molten body

(iv) casting said molten body containing the resultant dispersion by any desired means

wherein said first metallic material has a higher melting point than said second metallic material and is substantially insoluble therein.

2.) A method of preparing a metal alloy comprising a dispersion of particles of a first metallic material consisting of one or more refractory hard metals in a matrix of a second metallic material comprising the steps of :-

(i) establishing a molten body of said second metallic material

(ii) introducing into said body solid particles of a metalloid which reacts with said second metallic material to form particles of said first metallic material

(iii) stirring said molten body at a rate sufficient to effect shearing of the surfaces of the particles of said metalloid such that said surfaces are wetted by said molten body

(iv) casting said molten body containing the resultant dispersion by any desired means

wherein said first metallic material has a higher melting point than said second metallic material and is substantially insoluble therein.

3.) A method according to claims 1 or 2 wherein said molten body is established in an upright cylindrical vessel heated by any appropriate means and dispersion and wetting are achieved by one or more power driven impellers.

4.) A method according to claims 1 or 2 wherein said second metallic material is unalloyed aluminum, 5.) A method according to claim 1 wherein said second metallic material is unalloyed aluminum and said first metallic material is titanium diboride.

6) A method according to claim 1 wherein said second metallic material is unalloyed aluminum and said first metallic material is an aluminum boride,

7,) A method according to claim 2 wherein said second metallic material is unalloyed aluminum and said metalloid is elemental boron.

8.) A method according to any one of claims 1 through 7 wherein said molten body is maintained under vacuum.

9.) A method according to any one of claims 1 through 7 wherein said molten body is maintained under an atmosphere of argon gas.