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PREPARATION OF MAGNETIC MATERIALS AND MAGNETIC MEMBERS

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This invention relates to the preparation of magnetic materials and the making of magnetic members from such materials.

It has been known for some time that bismuth-manganese alloys are ferro-magnetic. Numerous investigators of bismuth-manganese alloys have worked out various procedures for preparing the alloys and also in producing magnetic members therefrom. However, considerable difficulty has been encountered in producing a satisfactory magnetic product. The specific MnBi alloy or compound appears to be the critical ferromagnetic material which it is desired to produce for magnetic purposes. However, it is extremely difficult to combine a quantity of manganese and bismuth under any known procedure so as to convert the two substantially completely to produce exclusively the MnBi alloy or compound.

It has been proposed to admix manganese and bismuth and melt them at high temperatures for prolonged periods of time under varying conditions of agitation and mixing. It has been well established, however, that only a portion of the manganese and bismuth reacts to form MnBi, and that a very appreciable portion of such mixtures comprises unreacted manganese and bismuth. As the temperature rises above about 271° C., at which bismuth melts, the particles of bismuth melt and rapidly collect into globules of progressively larger size and in a short time course, all of the bismuth forms a liquid pool on which the manganese floats. On further heating, eventually a temperature is reached, somewhat below the melting point of manganese, at which the manganese forms a mutual liquid solution with the bismuth. However, when this melt is cooled, it will precipitate out crystals of free manganese and on further cooling below the peritectic temperature, a small proportion of the entire mass converts to MnBi, the balance being unreacted manganese or bismuth or both. The precipitated free manganese, for example, is so intimately distributed throughout the MnBi crystallites that it has been found substantially impossible to separate them apart so as to yield MnBi crystals alone. Involved and costly procedures have been applied to the solidified product in order to isolate therefrom the portion comprising the MnBi crystallites, but such procedures, however, have not been successful in producing essentially a pure MnBi concentrate. Accordingly, it has not been feasible heretofore to secure reaction products comprising only crystals of magnetic MnBi free from non-magnetic manganese and bismuth.

The object of this invention is to provide for reacting manganese and bismuth in substantially equimolecular proportions under conditions whereby they react entirely to MnBi alloy.

A further object of the invention is to provide for producing a permanent magnetic material by embedding MnBi crystals in a binder and orienting the crystals in a magnetic field while the binder is hardened, thereby producing a magnet of optimum characteristics.

Other objects of the invention will, in part, be obvious and will, in part, appear hereinafter.

I have discovered that bismuth and manganese can be combined in substantially equimolecular portions and converted entirely into the magnetic alloy MnBi by heating an intimate mixture of suitably finely divided manganese and bismuth just below the melting point of bismuth. More particularly, a mixture of bismuth and manganese in equimolecular proportions, namely in a weight ratio of substantially 209 to 54.9, is ball milled for a period of hours until the particles are substantially all of a diameter of less than 44 microns and preferably all of a diameter of from 10 to 0.01 micron. The resulting intimate, ball milled mixture of bismuth and manganese is heated at a temperature slightly below 271.3° C., the melting point of bismuth, whereupon it reacts rapidly and substantially completely to the MnBi alloy or compound. Care must be used to keep the temperature during the reaction below the melting point of bismuth. In practice, the reaction of the finely divided powders is carried out at a temperature of between 260° C. and 271° C. Furthermore, the comminuting and heating of the manganese and bismuth must be carried out in the presence of a non-oxidizing or inert atmosphere such, for example, as nitrogen, argon, helium or the like, or in a vacuum. The powders are extremely sensitive to the presence of oxygen or other oxidizing substances, such as water and carbon dioxide, so that the powders will react spontaneously with the generation of substantial quantities of heat when a small quantity in an open test tube is exposed to the atmosphere.

In practicing the invention, substantially pure bismuth and manganese in proportions to provide equimolecular quantities are first crushed or otherwise reduced to moderately small particles, preferably in a non-oxidizing atmosphere. These particles may be of a size to pass through a screen having 20 meshes to the lineal inch, though it will be understood that the first subdivision may be coarser or finer than this. The roughly crushed materials are then placed within a ball mill provided with a nitrogen atmosphere, for example, and subjected to ball milling over a period of 8 to 24 hours, depending on the initial fineness of the particles, the size of the ball mill, and other factors. The ball mill may employ hardened metal balls, flint pebbles or the like. The ball milling should be such as to reduce the particles to a size of 10 microns in diameter and less. It will be appreciated that there may be present a few particles considerably larger than this diameter and that these may be readily removed by screening or the like. The ball milling not only reduces the particles but also intimately admixes the bismuth and manganese, so that it is in an intimately admixed condition suitable for subsequent reaction.

It will be understood that the bismuth and manganese may be separately ball milled, and that the suitably comminuted powders may be thoroughly admixed at the end of the ball milling operation. However, this entails a separate mixing operation which is avoided by a simultaneous ball milling operation. It is highly important that the bismuth and manganese particles be so treated that they are coated or smeared with each other.

The intimately admixed bismuth and manganese powders are then placed within a suitable enclosed furnace where they are subjected to temperatures not in excess of 271.3° C. I have secured good results by heating batches of the admixed powders following the schedule of bringing the powders from room temperature to 260° C. in ½ hour, then gradually increasing the temperature during

the next hour to 270° C., and then maintaining the mixture at 270° C. for at least an hour.

Reaction between the bismuth and manganese does not proceed at a usable rate below 260° C. In one test, after being heated for one hour at 260° C. the mixture had reacted to yield about 4% of the magnetic product, while at 265° C. for one hour about 15% of the mass had reacted to the magnetic MnBi. At about 270° C. the reaction proceeds so rapidly that it appears to require less than an hour to produce a complete conversion to MnBi.

It is extremely critical that the furnace at no time reach a temperature such that any of the bismuth melts. It has been discovered that molten bismuth has an extremely high surface tension, and that the particles of molten bismuth tend to collect into large globules which markedly resist complete reaction with the manganese. From numerous studies made by myself and other investigators in the art, it is a fact that once the bismuth in such a mixture has been melted, it reacts with manganese quite slowly and incompletely. As mentioned previously, reacting molten bismuth with manganese over periods of days at temperatures as high as 1200° C. failed to produce a complete conversion of the mixture to solid MnBi alloy crystals. In contrast thereto, by heating the manganese and bismuth powders to a temperature of just below the melting point of bismuth, for example, 270 to 271° C., I have obtained evidence that the reaction to solid MnBi crystals may be substantially complete in less than an hour. Equimolecular mixtures of bismuth and manganese reacted in accordance with the heating schedule of this invention contain substantially no unreacted bismuth or manganese. Therefore, there is no problem of separating undesired components from the desired highly magnetic MnBi crystals.

The reaction products produced by following the reaction schedule set forth herein are in powdered form though slightly agglomerated. It only requires a light working or ball milling of the reaction product in order to reduce it back to substantially the same type of fine powder, as present after ball milling. These finely divided powders, both before and after reaction, are highly reactive with oxygen or other oxidizing materials and, therefore, should be maintained at all times in an inert non-oxidizing atmosphere or even under vacuum.

In preparing magnetic members from the MnBi crystal powder of this invention, I admix a hardenable binder with sufficient of the powder so that the individual MnBi crystal particles are substantially separated from one another. The binders also function to protect the crystals from oxygen. The binders employed are liquid binders in which the MnBi crystals can be suspended or dispersed. Suitable liquid binders are the thermosettable resins. Low melting metals also can be employed. Good results have been secured by employing as binders polyester resins and epoxy resins. However, numerous other thermosettable and themoplastic compositions can be employed as binders. Thus, molten ethyl cellulose or cellulose acetate can be admixed with the MnBi powders, and upon cooling, the resin will harden to a solid.

It is necessary that the mixture of liquid binder and MnBi crystals be subjected to a magnetic field and maintained in the magnetic field until the binder has hardened. Under the influence of the magnetic field, the crystals of MnBi will orient in the desired direction and their magnetic axes will be maintained permanently in the oriented direction after the binder has been cured to its hardened state. A magnetizing field of the order of 4000 to 20,000 gauss, usually the highest field strengths will be employed, is adequate for orienting the MnBi crystals in producing permanent magnetic members therefrom.

The following is an example of the practice of the invention. Electrolytic manganese and chemically pure bismuth rough crushed to pass through a 20 mesh screen, are weighed out in the ratio of 54.93 grams of manganese and 209 grams of bismuth and placed in a ball mill employing steel balls, in which there is maintained a nitrogen atmosphere. After 16 hours of ball milling, there is produced a mixture of bismuth and manganese powders of a fineness such that all of the particles pass through a 325 mesh screen. Actually, the powders comprise particles of diameters of from 5 to less than 0.05 micron. The intimately ball milled mixture of powders is then placed in an evacuated sealed glass container and introduced into a furnace where the powders are heated rapidly from room temperature to 260° C. and then the temperature is slowly increased so that in the next ½ hour the temperatures reaches 265° C., and in the following ½ hour it rises to 270° C. The temperature of the powders is maintained just below the melting point of bismuth—approximately 270 to 271° C.—for 2 hours.

X-ray crystal defraction tests of the resulting reaction product showed that the powder comprised exlusively MnBi. There was no evidence of other compounds or of manganese or bismuth alone being present. The lattice constant C_0 was 6.119 and A_0 was 4.288 angstroms. The magnetic saturation in cgs units at 20° C. was 66 and the value extrapolated to 0° K. was 88. The magnetic saturation of the material of this invention is considerably superior to any material produced in the art heretofore.

The reaction product direct from the reaction furnace was lightly worked in order to break up the agglomerates. A quantity of the powder was then admixed with a liquid polyester resin while under nitrogen so as to provide approximately 65 volume percent of the powder and 35 volume percent of the resin. The polyester resin comprised a completely reactive solution of monostyrene and the unsaturated ester of propylene glycol and maleic anhydride. The mixture of powder and resin was placed in a mold about 2 inches in diameter and ½ inch in depth, and subjected to heating to cause the polyester resin to harden. Throughout this curing procedure the mixture was subjected to a magnetic field of 20,000 gauss until the resin had completely hardened. The resulting molded member was highly magnetic; the ${}_IH_c$ value was approximately 11,800 oersteds.

The pure MnBi crystal powders of the present invention have been used in producing permanent magnets having BH_{max} values of the order of 2×10^6, though theoretically it is possible to reach a value of as much as 18×10^6.

A number of mechanisms can be proposed for the successful reaction of manganese and bismuth in accordance with the present invention. One such is the probability that an intermediate stage occurs, which involves a eutectic containing about 2.2 mole percent of manganese which eutectic melts at about 265° C. This molten eutectic may coat the manganese particles and react therewith rapidly to form manganese bismuthide (MnBi). Regardless of the mechanism of the reaction I have found that the reaction in my process takes place most rapidly and completely at a temperature between about 265° C. and below the melting point of bismuth.

It will be appreciated that the present invention comprises a novel process for reacting manganese and bismuth, whereby to produce products comprising substantially entirely magnetic crystals of MnBi. Furthermore, the process is rapid and simple.

It will be understood that the above description and examples are illustrative and not limited.

I claim as my invention:

1. In the process of preparing a magnetic material from bismuth and manganese, the steps comprising intimately admixing powdered bismuth and manganese in equimolecular proportions, the powdered bismuth and manganese comprising particles of an average diameter of not over 10 microns, the particles of each material being coated or smeared with the other material and heating the admixed powders while in an unpressed condition in an inert atmosphere to a temperature just below

the melting point of bismuth but not less than 260° C. for a period of time whereby a product comprising substantially all highly magnetic MnBi alloy in a readily powdered form is produced.

2. The process of claim 1, wherein the powdered bismuth and manganese comprise ball milled particles substantially all of a diameter of between 0.01 to 10 microns.

3. The process of claim 1, wherein the admixing and heating takes place in an inert atmosphere.

4. The process of claim 1, wherein the admixing and heating takes place under a vacuum.

5. The process of claim 1, wherein the heating is between 270° C. and 271° C.

6. In the process of preparing a magnetic material from bismuth and manganese, the steps comprising ball milling a mixture of particles of a size of the order of 20 mesh of bismuth and manganese in the weight ratio of substantially 209 to 54.9, in the absence of oxygen and oxidizing materials, for a period of time of the order of hours to reduce substantially all the particles thereof to a diameter of less than 10 microns, the particles of each material being coated or smeared with the other material and heating the mixture of ball milled powder while in an unpressed condition under non-oxidizing conditions to a temperature just below the melting point of bismuth but not less than 260° C. for a period of the order of an hour whereby to produce a highly magnetic MnBi alloy in a readily powdered form.

7. In the process of preparing a magnetic member, from bismuth and manganese, the steps comprising ball milling a mixture of particles of a size of the order of 20 mesh of bismuth and manganese in the weight ratio of substantially 209 to 54.9, in the absence of oxygen and oxidizing materials for a period of time of the order of hours to reduce substantially all the particles thereof to a diameter of less than 10 microns, the particles of each material being coated or smeared with the other material and heating the mixture of ball milled powder while in an unpressed condition under non-oxidizing conditions to a temperature just below the melting point of bismuth but not less than 260° C. for a period of the order of an hour whereby to produce a highly magnetic MnBi alloy, admixing the MnBi alloy powder with a liquid binder, subjecting the mixture of powder and liquid binder to a magnetic field to orient the particles, and hardening the binder while the particles are so oriented.

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