

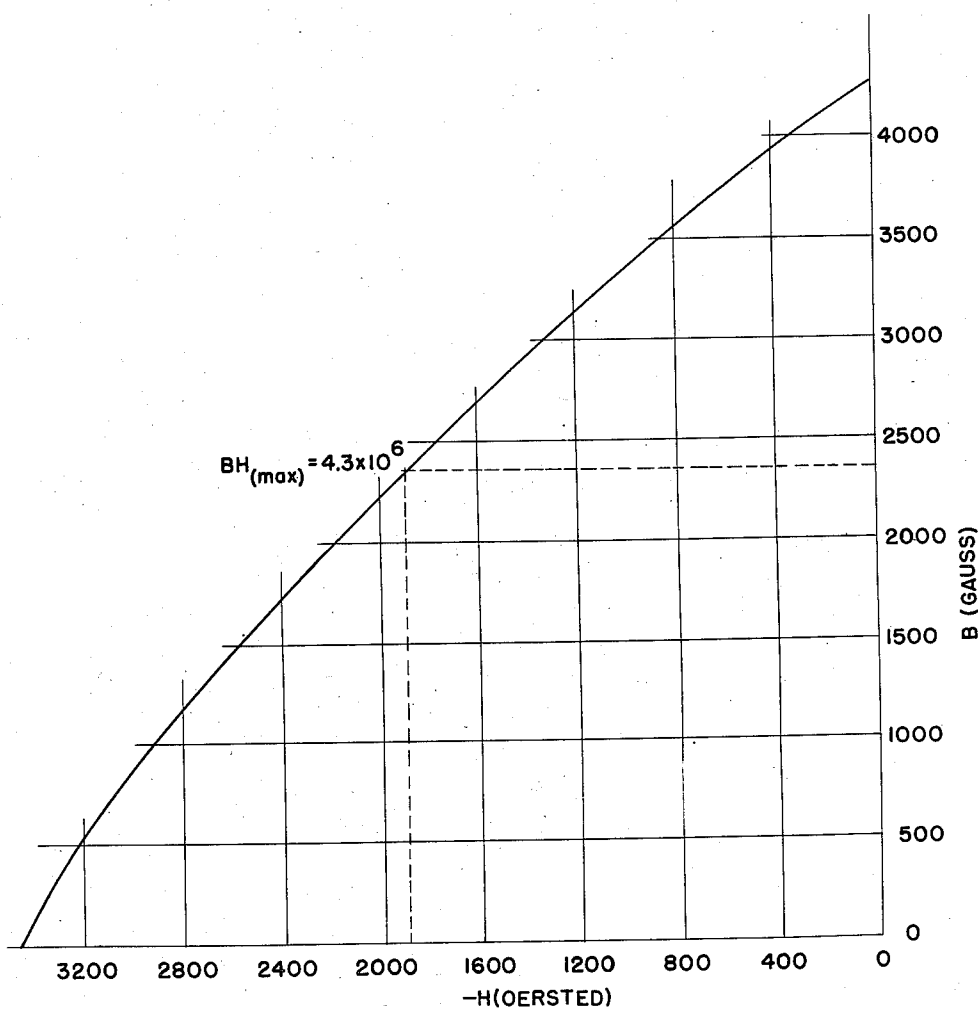
March 4, 1958

E. ADAMS ET AL

2,825,670

PERMANENT MAGNET AND PROCESS FOR MAKING SAME

Filed Aug. 21, 1952



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2,825,670

## PERMANENT MAGNET AND PROCESS FOR MAKING SAME

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Application August 21, 1952, Serial No. 305,718

(Granted under Title 35, U. S. Code (1952), sec. 266)

15 Claims. (Cl. 148—103)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention comprises novel and useful improvements in magnetic materials and more particularly pertains to improvements in permanent magnets and the method of making the same.

It is known that the intermetallic compound having the chemical composition MnBi possesses a high crystalline anisotropy and when in the powdered form in which the particles approximate domain size the compound exhibits a high coercivity and retentivity. However, when the compound manganese bismuthide is in a massive state, the elemental magnetic domains are oriented in complete randomness, and the compound possesses but low coercivity and remanence.

In order to produce a satisfactory permanent magnet from the compound manganese bismuthide, it is necessary to agglomerate the powdered manganese bismuthide with a suitable binder under the influence of an orienting magnetic field, which binder maintains the particles separate from each other, and which binder after solidifying retains the particles in the oriented positions established by the field. Manifestly, the quality of the magnet thus produced varies with the function of the ratio of the magnetic material to the total composition of the magnet including the binder and non-magnetic impurities, the quality of the magnet increasing as the aforementioned ratio increases subject to the limitations that the particles be maintained separate from each other.

In the preparation of the compound, the formation of the magnetic phase MnBi never proceeds to completion regardless of the initial proportions of manganese and bismuth present. When the initial charge consists of manganese and bismuth in equal atomic proportions according to the compound MnBi, the melt always consists of MnBi plus unreacted manganese in the matrix of bismuth. Complete separation of the magnetic phase MnBi from the bismuth cannot be readily achieved by known separation processes, and consequently the non-magnetic impurity bismuth will be present in the alloy utilized in making of the permanent magnet. In order to reduce the ratio of the non-magnetic materials to the total composition of the magnet, the instant invention provides for utilizing non-magnetic impurity, bismuth, as the matrix within which the magnetic particles having the chemical composition MnBi are suspended, the bismuth matrix serving to maintain the particles separate from each other and in the oriented position established by an external orienting field.

An important object of this invention is to provide a permanent magnet from the intermetallic compound having the chemical composition as given by the formula MnBi, which magnet has a high coercivity and retentivity.

Another object of this invention is to provide a permanent magnet from agglomerated manganese bismuthide

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having a high ratio of magnetic material to non-magnetic material.

Yet another object of this invention is to provide a magnet from powdered manganese bismuthide in which the unreacted bismuth, which is present due to the peritectic nature of the reaction of manganese and bismuth to form the intermetallic compound manganese bismuthide, is utilized as the matrix in which the powdered manganese bismuthide is suspended.

Still another object of this invention is to improve the orientation of the powdered manganese bismuthide particles in the direction of easy magnetization by superimposing an A. C. field on the D. C. orienting field, during the compaction of the material into a magnet.

A further object of this invention is to provide a magnet which can be readily formed into any desired size and shape, and when thus formed is mechanically and magnetically stable.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawing wherein the figure is a demagnetization curve for a magnet formed of manganese bismuthide powder and utilizing bismuth as the matrix.

The intermetallic compound having the chemical composition defined by the chemical formula MnBi is known to have a high crystal anisotropy of the order  $11.6 \times 10^6$  ergs cc. at 25° C., a high saturation magnetization and a Curie temperature of 340°–360° C. The composition manganese bismuthide is consequently well adapted for use in the preparation of a permanent magnet.

As hereinbefore set forth, the composition manganese bismuthide, when in its massive state, that is when the manganese bismuthide is in the form of crystals which are large as compared to the size of a single magnetic domain of the material, exhibits little or no ferro-magnetic characteristics because the magnetic domains are oriented in complete randomness and it is only when the material is comminuted into a fine powder of domain size that such characteristics are manifested. Best results in the production of a permanent magnet from manganese bismuthide can be achieved by comminuting the material into a powder of domain size, aligning all of the particles into their preferred direction of easy magnetization and compacting the powders to 100% density. In practice, 100% density cannot be achieved since the particles must be separated from each other.

The preparation of the compound manganese bismuthide is complicated by the fact that it is of the peritectic type, that is the formation of the magnetic phase MnBi never proceeds to completion regardless of the initial proportions of manganese and bismuth present. When the initial charge consists of manganese and bismuth in equal atomic proportion according to the compound MnBi, the melt always consists of MnBi plus unreacted manganese in a matrix of bismuth.

Any desired process for the preparation of MnBi may be utilized. One such method consists in the mixing of finely pulverized manganese and bismuth powders in approximately equal atomic proportions according to the compound MnBi, and placing the mixture in a crucible. The mixture is then positioned in a suitable furnace and heated to an elevated temperature such as 700°–1250° C. in a vacuum or under a protective atmosphere of an inert gas such as helium. The melt is maintained at this elevated temperature for a sufficient time to permit the reaction to proceed essentially to completion, or to any intermediate state desired. Due to the large difference in the respective densities and melting points of manganese and bismuth, the powdered manganese tends to float

upon the molten bismuth, and consequently provides only a small contact surface for the constituents to combine. It is therefore preferable that the heating be done in a rotating furnace in which the melt is continuously rotated during the heating at a low speed of about 20 R. P. M. Further, the speed of reaction may be improved if the melt is rotated about an axis which is inclined to the horizontal. The temperature of the furnace is then lowered preferably at a predetermined rate such as 65° C. per hour to a temperature such as 440° C. which is below the temperature of 453° C. above which the manganese bismuthide will not crystallize. At the last mentioned temperature, the rotation of the furnace is discontinued and the melt held at about 440° C. for a sufficient time to allow crystal growth to the extent desired. At the end of the above mentioned period, the melt is cooled to a temperature such as 320° C. at which time the furnace is rotated through 180° in order to place semi-solid mass of manganese bismuthide in the upper part of the crucible and allow any unreacted bismuth to drain out to the lower part of the crucible. This condition is maintained for a sufficient time to permit the above mentioned draining of the bismuth, and then the furnace is allowed to cool to room temperature or to a value which is sufficiently low to prevent oxidation of the mass upon removing it from the furnace.

In order to prepare a permanent magnet from manganese bismuthide, it is necessary to pulverize it into fine particles approaching domain size, that is particles of the order of 8000 Å. The pulverizing of the melt may be achieved by utilizing any known attrition process such as a high speed hammer mill. The resulting powder is extremely pyrophoric and consequently the pulverizing must be done in a vacuum or in an atmosphere of an inert gas such as helium.

As hereinbefore mentioned, the reaction of manganese and bismuth to form the compound manganese bismuthide is of the peritectic type and the resulting melt consists of MnBi plus unreacted manganese in the matrix of bismuth. Since the quality of the magnet is improved by utilizing a magnetic material that is relatively pure, it is desirable, but not essential to the production of a magnet, to further enrich the melt by separating as much non-magnetic constituents from the reacted MnBi as is desired for higher quality magnets, complete separation thereof, as aforesaid, being unattainable by known separation processes. The amount of unreacted bismuth present in the pulverized mass used to make the magnet is not a critical limitation but is a matter of choice depending upon the quality of magnet desired. In other words, enrichment of the melt is optional at the discretion of the designer, since the pulverized mass, as is and when subjected to the steps hereinafter described, could be utilized to produce a magnet; and, if the enrichment operation is employed in the process herein described to obtain a higher quality magnet, the degree of separation is selective, depending on the quality of magnet desired to be obtained. The separation of the magnetic phase MnBi from the manganese and bismuth can be achieved by using a magnetic separator after comminuting the melt. However, whatever the process used for separating the magnetic phase MnBi from the non-magnetic phase, small particles of unreacted bismuth tend to cling to the particles of the manganese bismuthide. The essence of the instant invention is the utilization of these clinging unreacted bismuth particles, in lieu of plasticizers or foreign material, as the binder for the formation of the magnet, thereby reducing the ratio of non-magnetic materials to the total composition of the magnet.

To protect the powder from oxidation, the separation is preferably carried out under a protective atmosphere.

It is to be understood, however, that the foregoing process for the preparation of the enriched manganese bismuthide powder is exemplary only. For example, the melting of the manganese and bismuth may be achieved

by dissolving the manganese in molten bismuth at about 270° C. Further, the melt may be enriched by filtering, decanting or centrifuging of the hot melt either before or after comminuting the latter.

In the preparation of a permanent magnet from the manganese bismuthide particles, the instant invention provides for utilizing the unreacted bismuth, which as heretofore set forth cannot be readily separated from the manganese bismuthide, as the matrix in which the manganese bismuthide particles are suspended. The pulverized mass, either before or after the enrichment, may be classified as by sieving through a screen of the order of 325 mesh, so as to obtain only particles of small sizes. The enriched powder is then compacted at a temperature between the melting point of bismuth [273° C.] and the Curie temperature of manganese bismuthide which is 340° C.-360° C. For example, the compaction may be carried out in a heated die, which is loaded under a protective inert atmosphere, at a temperature of 300° C.

The compaction is preferably carried out in a moderately high orienting magnetic field such as 10,000 to 12,000 oersteds to provide alignment of the particles in the preferred direction of easy magnetization, although the compaction can be carried out in relatively lower orienting fields with a consequent reduction in orientation of the particles. Due to the fact that the compaction operation is carried out at a temperature above the melting point of bismuth, the unreacted bismuth, which is still present in the powdered melt, is in a molten state and thus provides a fluid medium in which the manganese bismuthide particles are suspended to thereby facilitate alignment of the manganese bismuthide particles. Alignment of the particles may further be facilitated by subjecting the melt to any one of several "shaking" procedures while the melt is under the influence of the orienting magnetic field. A preferable method of carrying out the "shaking" procedure is the utilization of an A. C. "shaking" field superimposed upon the D. C. orienting field so as to agitate the particles and break up the particle clusters which are formed due to the permanent magnet of the manganese bismuthide particles. As is readily obvious to those skilled in the art, in order for the D. C. magnetic field to be the dominating field so as to align the particles in the desired direction the peak magnitude of the A. C. agitating field must of necessity be less than the magnitude of the D. C. magnetic field. The A. C. "shaking" field thus serves to facilitate the alignment of the manganese bismuthide particles in the preferred direction of easy magnetization. It is to be understood that, in lieu of the aforesaid superimposed A. C. fields "shaking" method, any other means of "shaking" could be used to effect alignment of the particles, such as ultrasonic or mechanical vibrations. When cooled, the bismuth solidifies and immobilizes the manganese bismuthide particles.

The resulting compact is then magnetized, either before or after assembly to auxiliary equipment such as mounting brackets, pole pieces or leakage paths, and then stabilized in any manner known to the art.

During compaction at temperatures above the melting point of bismuth and below the Curie point of manganese bismuthide, and at relatively high pressures of the order of 3,000 p. s. i., any liquid bismuth in the compact in excess of that necessary to form a matrix for the manganese bismuthide particles is forced out between the ram and the die. Thus, compaction of the powdered manganese bismuthide at the temperature and pressure ranges set forth above not only permits the use of the bismuth impurity already present in the melt as the matrix, but in addition serves to further enrich the magnet.

As an example of the method of preparing the magnetic material manganese bismuthide, and the production of a magnet therefrom, powdered manganese and bismuth were mixed together in the proportions 16.7% manganese and 83.3% bismuth, which mixture was heated for five hours

at 700° C. in a helium atmosphere. The temperature was then lowered to 440° C., and this temperature was maintained for 16 hours after which the material was allowed to cool to 320° C. at which temperature the bismuth was decanted from the manganese bismuthide crystals. After cooling to room temperature, the resulting mass was pulverized under a helium atmosphere to an average particle size of approximately 8 microns, passed through a 325 mesh screen and separated by magnetic means in an atmosphere of carbon dioxide. The resulting powder was then compacted in a pulsing magnetic field of from 10,000 to 12,000 oersteds at a temperature of approximately 300° C. under a pressure of approximately 3,000 p. s. i., into a cylindrical pellet having a density of 8.0 grams per cc. The pellet was found to have the following magnetic characteristics as obtained from the demagnetization curve of the specimen illustrated in Fig. 1:

Residual magnetization  $[B_r] = 4350$  gauss.

Coercive force  $[H_c] = 3460$  oersteds.

BH  $[max] = 4.3 \times 10^6$  gauss-oersteds.

Density = 8.0 g. cc.

Whereas a high quality magnet has been described as being produced under a compacting pressure of the order of 3,000 p. s. i., relatively good-permanent magnets have been produced utilizing comparatively low compacting pressures of the order of 100–200 p. s. i. However, high compacting pressures are advantageous in that the compact is further enriched by expression of the excess molten bismuth.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. The method of making a permanent magnet comprising forming a mass consisting of substantially only bismuth and particles of the compound manganese bismuthide, comminuating the mass, compacting the comminuted mass in an orienting magnetic field at a temperature above the melting point of bismuth and below the Curie point of said compound whereby the manganese bismuthide particles are suspended in a fluid medium constituted of substantially only bismuth thereby to facilitate the influencing effect of the orienting magnetic field on said particles, cooling the resulting compact to solidify the bismuth to form an agglomerate in which substantially only the solidified bismuth constitutes the binder for the manganese bismuthide particles, and submitting the agglomerate to a magnetizing field.

2. The method of making a permanent magnet comprising reacting manganese and bismuth in such proportions as to produce a mass consisting of particles of the compound manganese bismuthide and substantially only unreacted bismuth, comminuating the mass, compacting the comminuted mass in an orienting magnetic field at a temperature above the melting point of bismuth and below the Curie point of said compound whereby the manganese bismuthide particles are suspended in a fluid medium constituted of substantially only bismuth thereby to facilitate the influencing effect of the orienting magnetic field on said particles, cooling the resulting compact to solidify the bismuth to form an agglomerate in which the solidified bismuth solely constitutes the binder for the manganese bismuthide particles, and submitting the agglomerate to a magnetizing field.

3. The method of making a permanent magnet comprising reacting manganese and bismuth in such proportions as to produce a mass consisting of particles of the compound manganese bismuthide and substantially only unreacted bismuth comminuating the mass, compacting the comminuted mass in an orienting magnetic field at a temperature above the melting point of bismuth and below

the Curie point of said compound whereby the manganese bismuthide particles are suspended in a fluid medium of substantially only bismuth and at a pressure high enough to bring said particles into mutual close proximity and squeeze out the excess fluid medium of bismuth, cooling the resulting compact to solidify the remaining bismuth to form an agglomerate in which the solidified remaining bismuth solely constitutes the binder for the manganese bismuthide particles, and subjecting the agglomerate to a magnetizing field.

4. In the process of making permanent magnets from a comminuted mass consisting of substantially only unreacted bismuth and particles of the compound manganese bismuthide, the operation comprising compacting the comminuted mass at a temperature above the melting point of bismuth and below the Curie point of said compound whereby the manganese bismuthide particles are suspended in a fluid medium consisting of substantially only bismuth and simultaneously applying a direct current orienting magnetic field and alternating current agitating magnetic field having a peak magnitude less than said direct current field.

5. The process of claim 4 wherein the pressure applied during compacting of the comminuted mass is high enough to bring the manganese bismuthide particles into mutual close proximity and squeeze out the fluid medium of bismuth in excess of the amount desired to bind the manganese bismuthide particles in an agglomerate.

6. The method of making a permanent magnet comprising reacting solely manganese and bismuth in such proportions as to produce a mass consisting of particles of the compound manganese bismuthide dispersed in unreacted constituent material, extracting a portion of the unreacted material to decrease the ratio of unreacted material to the total composition of the mass, the remaining portion of the unreacted material solely serving as the matrix for the manganese bismuthide particles to form a composite body, orienting the manganese bismuthide particles in the composite body in the direction of easy magnetization, and submitting the composite body to a magnetizing field.

7. The method of making a permanent magnet comprising reacting solely manganese and bismuth in such proportions as to produce a mass consisting of magnetic phase particles of the compound manganese bismuthide dispersed in non-magnetic unreacted constituent material, magnetically enriching the mass by selectively extracting a portion of the non-magnetic unreacted material, the remaining unreacted material solely binding the manganese bismuthide particles to form a composite body, orienting the manganese bismuthide particles in the composite body in the direction of easy magnetization, and submitting the composite body to a magnetizing field.

8. The method of making a permanent magnet comprising reacting solely manganese and bismuth in equal atomic proportions at elevated temperatures to produce a mass consisting of magnetic phase particles of the compound manganese bismuthide dispersed in non-magnetic unreacted constituent material, magnetically enriching the mass by selectively extracting a portion of the non-magnetic unreacted material, orienting the manganese bismuthide particles in the direction of easy magnetization at a temperature below the Curie point of said compound but at a temperature sufficient to cause the unreacted material to become slushy whereby the manganese bismuthide particles are suspended in a slushy medium of solely unreacted material thereby facilitating the orienting of the manganese bismuthide particles, solidifying the unreacted material present in the enriched and oriented mass to form an agglomerate in which the solidified unreacted material solely constitutes the binder for the manganese bismuthide particles, and subjecting the agglomerate to a magnetizing field.

9. The method of making a permanent magnet comprising reacting solely manganese and bismuth in such

proportions at elevated temperatures as to produce a peritectic melt consisting of semi-solid particles of the compound manganese bismuthide dispersed in fluid unreacted constituent material, enriching the melt by draining out a desired portion of the fluid unreacted material, cooling the enriched melt to form a mass, comminuting the mass, compacting the comminuted mass in an orienting magnetic field at temperature below the Curie point of said compound but at a temperature sufficient to cause the unreacted material to become slushy whereby the manganese bismuthide particles are suspended in a slushy medium of solely unreacted material thereby facilitating the influencing effect of the orienting magnetic field on said particles, cooling the resulting compact to solidify the unreacted material present therein to form an agglomerate in which the solidified unreacted material solely constitutes the binder for the manganese bismuthide particles, and subjecting the agglomerate to a magnetizing field.

10. The method of claim 9 wherein the comminuted mass is enriched prior to compaction by extracting the portion of unreacted material in excess of the amount desired to form a sufficient fluid medium in which to suspend the manganese bismuthide particles.

11. The method of claim 10 wherein the pressure applied during compacting of the comminuted mass is high enough to bring the manganese bismuthide particles into mutual close proximity and squeeze out the slushy medium of unreacted material in excess of the amount desired to bind the manganese bismuthide particles in an agglomerate.

12. The method of claim 10 wherein the comminuted mass is subjected to agitating vibrations while under the influence of the orienting magnetic field to disrupt clusters

of manganese bismuthide present in the comminuted mass.

13. The method of making a permanent magnet comprising reacting solely manganese and bismuth in such proportions as to produce a mass consisting of magnetic phase particles of the compound manganese bismuthide dispersed in non-magnetic unreacted constituent material, comminuting the mass, compacting the comminuted mass in an orienting magnetic field at a temperature above the melting point of bismuth and below the Curie point of said compound, cooling the resulting compact to solidify the unreacted material present therein after compaction to form an agglomerate in which the solidified unreacted material solely constitutes the binder for the manganese bismuthide particles, and subjecting the agglomerate to a magnetizing field.

14. The method of claim 13 wherein the comminuted mass is subjected to agitating vibrations while under the influence of the orienting magnetic field to disrupt clusters of manganese bismuthide present in the comminuted mass.

15. A magnetic composition for use as a permanent magnet consisting of particles of the compound manganese bismuthide, which particles have been formed by the peritectic reaction of combining solely manganese and bismuth in equal atomic proportions at elevated temperatures, suspended in a predetermined direction of magnetization in a matrix composed solely of unreacted material from said peritectic reaction.

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