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3,073,728

MAGNETIC MATERIALS

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This invention relates to fine particle magnets having a lead matrix and to a process for preparing such magnets.

The manufacture of elongated magnetic particles, having transverse dimensions which are those of a single magnetic domain, by plating a magnetic material into a molten metal cathode is described in copending application, Serial No. 500,078, filed April 8, 1955, now U.S. Patent 2,974,104, and assigned to the same assignee as the present invention. These magnetic particles represent a significant advance over prior magnetic materials which were largely spheroidal or relatively blunt magnetic particles.

Copending application, Serial No. 702,803, filed December 16, 1957, now U.S. Patent 2,999,778, and assigned to the same assignee as the present invention, describes a lead, or lead containing up to a maximum of about 2 percent or less by weight of antimony, matrix for the fine particle magnetic material. The lead or lead-antimony matrix for the fine particle magnetic material provides a nonreactive carrier for the magnetic particle and serves to protect the particles from the effects of oxidation, during removal of the mercury. The lead or lead alloy matrix also provides a physical spacer or carrier for the particles, and possesses other advantageous features.

When the finished fine particle magnets containing such a lead matrix are exposed to temperatures above about 100° C. for prolonged periods of time, large areas on the surface of the magnets often become covered with whiskers, some of which are about 1/16 in. in length. These whiskers are composed of lead. For certain applications, the whiskers which form on the fine particle magnets are not detrimental. However, for other purposes, such whisker growth cannot be tolerated. For example, these whiskers can impinge upon moving components, such as the disk which rotates through the damping magnet in a watt-hour-meter. These whiskers are observed on magnets which have been temperature aged in both air or vacuum, although the growth occurs faster and more densely under vacuum conditions.

A principal object of the present invention is to provide a matrix for fine particle magnetic materials which is not subject to the disability of whisker growth under heating conditions. An additional object of the present invention is the provision of a relatively simple method for the prevention of whisker growth in fine particle magnetic materials having a lead or lead-alloy matrix.

It has been discovered that the addition of 0.09 part by weight or more of cadmium metal to each part by weight of the lead matrix in which the magnetic particles are imbedded completely eliminates whisker growth in such magnets. A possible explanation for the growth of whiskers on the surfaces of the magnets is that such whisker growth results from the recrystallization of lead or lead-antimony at the elevated temperatures employed in pressing or extruding the magnets. If recrystallization occurs, elevation of the recrystallization temperature of the

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lead by the addition of a metal should eliminate whisker growth. It has, however, been found that cadmium is the only metal which both eliminates whisker growth and does not deleteriously affect the remaining properties of the magnet. Other metals, metallurgically similar to cadmium, either do not eliminate whisker growth or attack the magnetic particles of the magnet, or in some cases, both.

In general the magnetic structures of the present invention comprise finely divided particles of magnetic material and a lead-containing matrix, the matrix containing at least 0.09 part by weight of cadmium for each part by weight of lead.

In the aforementioned copending application, Serial No. 702,803, it is pointed out that the lead matrix may be added to the magnetic particles as elemental lead in the form of chunks or pellets, or as a mixture of lead and mercury. The matrix material is added to the fine particle magnetic material—mercury slurry. If desired, the fine particle magnetic material can be coated with an antimonide in accordance with the disclosure of copending application, Serial No. 702,801, filed December 16, 1957, now U.S. Patent 2,999,777 and assigned to the same assignee as the present invention. It is preferable to form the antimonide on the magnetic particles after the addition of the lead matrix material, rather than before, although it may be added either before or after. The amounts of antimony to be added to the magnetic particle mercury slurry and other processing details of coating with the antimonide are more fully set forth in the aforesaid copending application, Serial No. 702,801.

In accordance with the aforementioned copending applications, the magnetic material as the anode is plated into a molten metal cathode. Elongated magnetic particles are produced having a median elongation ratio of at least 1.5 to 1 and having at least one half of the particles possessed of an elongation ratio of at least 2 to 1. The particle-molten cathode slurry is then heated for a few minutes at about 150–200° C. and cooled.

Before distilling or washing the mercury or other molten metal cathode from the slurry, it is preferable to compress the material in a non-magnetic compacting mold or die while subjecting it to a magnetic field. The purpose of this step is to align the elongated iron or other magnetic particles in the direction of the magnetic field to obtain the optimum ratio of residual to saturation induction, and to maintain the aforesaid ratio during the removal of mercury by distillation. Conveniently, the pressure used in this compacting step is 3000 p.s.i. or higher, preferably 10,000 p.s.i., and the impressed magnetic field has a strength of 4000 gauss or higher. This step also serves to remove some of the mercury.

The remaining mercury is preferably removed from the mixture by vacuum distillation at an elevated temperature. The iron antimonide layer on each particle allows this operation to be carried out without spheroidizing the magnetic particles and degrading their magnetic characteristics. In general, the temperature of distillation is 300° C. to 400° C., the pressure less than 1 mm. of mercury, and the time of distillation from 1 to 12 hours depending on the size of the compact. After the vacuum distillation, the magnetic material contains up to about 4% by weight of residual mercury, which amount cannot be substantially lowered by various al-

terations in the operation conditions and may be considered essentially mercury-free.

The final step in the preparation of a finished or complete magnetic structure consists of grinding up the more or less porous mass of iron or other fine particle magnetic material, antimony and lead, which remains after the vacuum distillation process, and pressing it in a directionalizing magnetic field employing conventional powder metallurgy techniques, using typically a pressure of about 50,000 p.s.i., and, if an oriented magnet is desired, a magnetic directionalization field of about 4000 gauss or more. Alternatively, the mass remaining after the vacuum distillation process can be pressed hot at a temperature of about 350° C. and at pressures from 3000 to 50,000 p.s.i., preferably 18,000 p.s.i., to flow the lead binder into position, at the same time maintaining a directionalizing field of about 4000 gauss on the material if orientation is desired.

It is important to note that the whisker growth does not generally occur unless the fine particle magnetic material is pressed into a magnetic structure at elevated temperatures. Thus, the problem of whisker growth occurs whenever the fine particle magnetic structures are hot pressed, extruded, or hot rolled. A magnet is hot-pressed rather than cold-pressed, where a high magnetic packing fraction is necessary (ordinarily, if the packing fraction is to be 0.40 or greater), or where greater physical strength or environmental stability is desired.

The cadmium added in accordance with the teachings of the present invention may be added at the same time that the lead or the lead-antimony alloy is added. It may be added either as pure cadmium or as an alloy of lead and cadmium. The cadmium itself is soluble in molten lead and therefore mixes well. An advantage of the present invention resides in the fact that the addition of amounts even as small as 0.09 part by weight of cadmium to the lead matrix lowers the melting point of the lead. Thus, the magnetic structure can be hot-pressed, for example, at a temperature lower than it could have been hot-pressed in the absence of cadmium. Thus, the present invention improves the hot-pressing characteristics and consequently the stability of the finished magnets.

The following example will illustrate the preparation of a magnetic structure in accordance with the practice of the present invention.

EXAMPLE 1

A mercury slurry of fine particle iron prepared as disclosed in the above co-pending application, Serial No. 500,078, was heat-treated for 14 minutes at 175° C. The slurry, prior to heat treatment, contained 96.5 lbs. of mercury and 3.5 lbs. of iron particles. While still hot, 6.5 lbs. of lead as a matrix material, 0.50 lb. of antimony as a coating material, and 0.65 lb. of cadmium were added to the slurry. The resultant mixture was heat-treated for an additional period of 15 minutes at 175° C. After cooling, the mixture was pressed at a pressure of 10,000 p.s.i. in a non-magnetic mold in the presence of a D.C. magnetic field of 4000 gauss to align the elongated iron particles in the direction of the field, to form preforms of the particles and to reduce the mercury content to about 80%. Essentially all of the rest of the mercury was then removed by distilling the material at a pressure of about 1 mm. of mercury for 4 hours at 350° C. This reduced the mercury to about 2% by weight of the preform. The preforms were then ground in a rotary cutter and completely mixed to yield a powder of uniform consistency having a mesh size of from -10 to +400. The magnetic powder was then hot-pressed at a temperature of 350° C. and a pressure of 18,000 p.s.i.

The above example was repeated adding successively varying amounts of cadmium to the lead forming the

matrix for the magnetic structure. The amounts varied from 0.09 part for each part by weight of lead, to 0.68 part. The resulting magnets were then aged in air and vacuum at 150° C. for 6 weeks. It was found that no whiskers could be observed on the resulting aged magnets. Although the addition of lower amounts of cadmium to the lead matrix retards whisker growth, it has been found that less than about 0.09 part by weight of the cadmium per 1 part by weight of lead does not completely eliminate whisker growth. There is no upper limit on the amount of cadmium which may be used, although there is obviously no need to add a relatively expensive material such as cadmium in large amounts, if small amounts are operative to eliminate whisker growth.

In order to determine whether the present invention is specific to cadmium, a series of tests were carried out using other metallic materials which were soluble in the mercury cathode. These included tin, bismuth, silver, and zinc. It should be noted that any material added to the lead matrix must be soluble in the molten metal cathode. In addition, the added material should not be one which forms alloys with the lead matrix material which will raise the melting point of the matrix. Otherwise the magnetic materials will be damaged when they are hot-pressed. Each of the metallic materials tested was used in amounts of 0.10 part by weight per each part by weight of the lead forming the matrix. The metals were selected because they were soluble in both lead and mercury. After aging these magnets for 7 weeks at 150° C., the following results were observed:

Table A

Additive to Lead Matrix	Results	
	Whisker Growth	Attack of Iron Particles
Tin.....	Very slight.....	Severe.
Bismuth.....	Slight.....	None.
Silver.....	Very slight.....	Severe.
Zinc.....	do.....	do.
Cadmium.....	None.....	None.

The above table demonstrates that materials, other than cadmium, either do not eliminate whisker growth, result in attack of the fine particle magnetic material, or both.

It will therefore be seen that the present invention provides a relatively simple and effective means for preventing whisker growth on fine particle magnetic materials which are imbedded in a lead matrix in the final magnet structure. In addition to iron, which has been specifically illustrated, the present invention is applicable to magnetic structures formed from other magnetic materials, such as cobalt and nickel and alloys formed from iron, cobalt and nickel.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A magnetic structure comprising finely divided particles of magnetic material selected from the group consisting of iron, cobalt, nickel and alloys containing iron, cobalt and nickel, and a matrix material selected from the group consisting of lead and a lead-antimony alloy, said matrix containing at least 0.09 part by weight of cadmium per part by weight of the lead.

2. A magnetic structure comprising finely divided particles of magnetic material selected from the group consisting of iron, cobalt, nickel and alloys thereof, and a matrix material selected from the group consisting of lead and a lead-antimony alloy containing up to 2% by weight antimony, said matrix containing at least 0.09 part by weight cadmium per part by weight of the lead.

3. The magnetic structure of claim 2 in which the finely divided particles of magnetic material are coated with the reaction product of antimony and said material.

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4. A magnetic structure comprising finely divided particles of iron, said particles being coated with the reaction product of antimony and iron, and a matrix material selected from the group consisting of lead and a lead-antimony alloy containing up to 2% by weight antimony, said matrix containing at least 0.09 part by weight cadmium per part by weight of the lead.

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