United States Patent [19]
Haberer
[11] 3,844,851
[45] Oct. 29, 1974

[54] PRE-FITTING METHOD OF MANUFACTURING COBALT SAMARIUM PERMANENT MAGNET ALLOY

[75] Inventor: **Jean-Paul Haberer**, Saint Martin d'Heres, France

[73] Assignee: **Societe d'Etudes et de Recherches Magnetiques (SERMAG)**, Saint Martin d'Heres, France

[22] Filed: **Apr. 19, 1973**

[21] Appl. No.: **352,695**

[30] **Foreign Application Priority Data**

May 2, 1972 France 72.15499

[52] **U.S. Cl.** **148/103**, 148/31.57, 148/105, 148/108

[51] **Int. Cl.** **H01f 1/02**

[58] **Field of Search** 148/103, 31.57, 105, 108, 148/102, 101

[56] **References Cited**

UNITED STATES PATENTS

3,523,836	8/1970	Buschow et al.	148/31.57
3,684,499	8/1972	Hofer et al.	148/101
3,684,593	8/1972	Benz et al.	148/102
3,748,193	7/1973	Cech	148/101
3,755,007	8/1973	Benz et al.	148/31.57

Primary Examiner—Walter R. Satterfield
Attorney, Agent, or Firm—Cushman, Darby & Cushman

[57] ABSTRACT

Method of manufacturing a material for permanent magnets based on samarium and cobalt, of the type consisting of preparing a powder of an alloy of these two bodies, compacting this powder under high pressure, at the same time applying to it a magnetic field orienting the magnetic particles in the alloy, then applying a thermal treatment to the pieces obtained said thermal treatment, comprising a pre-fritting step carried out at a temperature of between 600° and 1000°C and preferably around 750°C, followed by the conventional sintering and annealing steps.

4 Claims, No Drawings

PRE-FITTING METHOD OF MANUFACTURING COBALT SAMARIUM PERMANENT MAGNET ALLOY

The invention relates to the manufacture of permanent magnets from a samarium cobalt alloy.

It is known that such manufacture, on an industrial scale, gives rise to considerable practical difficulties. It has proved impossible, in particular, to carry out direct fritting of the definite compound Sm Co_5 (which has the best magnetic properties). In effect, surface evaporation of the samarium occurs, leading to the formation around the grains of Sm Co_5 alloy of a film rich in cobalt (a compound of the Sm_2 Co_{17} type which does not have good permanent magnet properties) which shunts each of these grains, thus spoiling the magnetic properties of the material. Moreover, this film has a high melting point and hinders fritting.

To overcome this difficulty, it has been suggested that respective samarium and cobalt contents corresponding to the formation of Sm Co_5 and Sm_2 Co_7 compounds be used for the alloy. For this purpose, a samarium content of about 34 to 42 percent by weight is used.

A known method which is based on such a composition consists of compacting a powder of said alloy under high pressure, at the same time applying to it an orientating magnetic field, then applying a thermal treatment to the pieces obtained, comprising fritting at a temperature of about 1100°C.

In this method, efforts are made to avoid thermal shocks, so the pieces are slowly heated to fritting temperature, then slowly cooled to ambient temperature.

The applicant has discovered that this thermal cycle was not the one which allowed the best possible magnetic properties to be obtained from the material.

In accordance with the invention, a pre-fritting operation at a temperature of between 600° and 1000°C and preferably around 750°C is included in the above-mentioned thermal treatment.

The effect of this pre-fritting is to increase the density of the residual induction of the end product. It is moreover known that an annealing operation carried out after cooling the fritted pieces improves their intrinsic coercive field and induction and that the magnetic characteristics of the end product depend to a large extent on the greater or lesser rapidity with which the pieces are removed from the annealing furnace. In practice, the annealing operation will be, after rapid removal of the pieces, immediately followed by sudden water quenching.

The coercive field of the end product is thereby considerably improved.

A better understanding of the invention will be obtained from the following description of a preferred method of implementation of the method.

An alloy made up of samarium and cobalt is prepared, the latter material having a purity of about 99.95 percent. The samarium is in the form of fibres and it is first remelted to form a compact bar. The initial proportions are between 35 and 42 percent of samarium by weight, the preferred samarium content being around 37 percent.

For example, a charge of 700 g. comprising 259 g of Sm and 441 g of Co is treated. Melting is done in an induction furnace supplying 30 kW power at a frequency of 4 KHz, preferably in accordance with the method described in U.S. Pat. application filed on December 10, 1971 under the Ser. No. 206,732 by the inventor. for: "Method and device for manufacturing alloys of transition elements and rare earth group metals intended for the production of materials for permanent magnets."

This method consists of first melting the Co, placed in a recrystallized alumina crucible, by heating to about 1500°C, leaving it to cool to about 1100°C, then lowering a bar of Sm into contact with the contents of the crucible: Sm diffuses in Co. When the alloying operation is finished, the alloy is reheated for about one minute to liquefy and homogenize it, then it is cast in a graphite ingot-mould.

The material obtained is then pounded, then crushed into a powder whose grain size, measured by means of a FISHER SUB-SIEVE instrument, is about 4 microns. The intrinsic coercive field of this powder, measured after saturation in a 95,000-Oersted field, is about 10,000 Oersteds. This powder is mixed with a lubricant to facilitate its subsequent compression, then premagnetized in a pulse field in accordance with the method described in French Patent application filed on Oct. 29, 1970 under the serial number 70.39.028 by "SOCIETE D'ETUDES ET DE RECHERCHES MAGNETIQUES."for: "Improvement to the methods of manufacturing materials for permanent magnets."

The material is then shaped into a cylinder by compressing the powder under a pressure of about $2T/cm^2$ in the presence of a magnetic field parallel to the direction of compression, with an intensity of 10 to 15 Koersteds.

The compressed cylinder coming out of the press has the following characteristics:

density 5.25 (i.e., 62 percent of the theoretical density in the mass state)

residual induction Br = 4,000 Gauss

induction BHc = 4,000 Oersteds.

The compressed pieces are piled in a refractory shuttle made e.g. of stainless steel and coated with a powder of an auxiliary samarium alloy with a melting point higher than that of the basic alloy in accordance with the method described in U.S. Pat. application filed on Dec. 21, 1971, Ser. No. 210,583 for: "Method of manufacturing fritted permanent magnets on basis of cobalt and rare earths," by the Inventor.

The shuttle is then inserted into a refractory tube (e.g. made of quartz) sealed at one end and the other end of which is connected to a pumping unit.

This quartz tube is emptied of its air until a primary vacuum is obtained, keeping it at a temperature of about 200°C, then an inert gas is introduced into it, such as helium or argon, under a pressure of 1 atmosphere.

A pre-fritting operation is then carried out in the following way:

the quartz tube is introduced into a furnace maintained at a temperature of between 600° and 1000°C and preferably around 750°C for a period of 2 to 60 minutes, preferably 20 minutes.

This operation makes it possible to obtain a higher final density after fritting and a higher residual induction than those obtained in the standard way, without pre-fritting.

Thus, a piece fritted at 1115°C for 30 min., without pre-fritting, has the following characteristics:

density: 88 percent of the theoretical density
Br = 6,800 Gauss

Pre-fritting at 750°C for 20 min., followed by the same fritting as above gives:

density: 94 percent
Br: 7,250 Gauss.

This pre-fritting thus constitutes an important characteristic of the method in accordance with the invention. Moreover, it gives a material which is already cohesive enough to allow it to be machined. Machining can therefore be done at this stage of manufacture more easily than in the final stage, where the pieces have much greater density.

It is followed by fritting carried out in the following way. The temperature of the quartz tube is raised, in about 10 minutes, from 750° to a value of between 1050° and 1150°C. More specifically, this is achieved by moving the quartz tube slowly from one area to another in the same furnace. The pieces are maintained at fritting temperature (second furnace area) for 10 to 60 minutes. The quartz tube is then quickly brought out into the ambient air and left to cool naturally.

The pieces then have the following characteristics:

density: 94 percent
Br = 7,900 Gauss
Hc = 4,600 Oersteds
Max.product (BH) = 14.5 Megagauss × Oersteds (MG.Oe).

An annealing operation is then carried out which is known in itself and of which it is known that it considerably improves the values of the intrinsic coercive field and the induction. This operation is effected in the following way:

The pieces are again coated with the above-mentioned auxiliary alloy and the shuttle, after primary pumping, is placed in a helium atmosphere in a refractory stainless steel tube. This tube is introduced into a furnace and maintained for a period of 5 to 48 hours - preferably 24 hours - at a temperature lower than the fritting temperature, e.g. 900°C.

The characteristics of the pieces then assume the following values:

density: 94 percent
Br = 7,900 Gauss
Hc = 5,500 Oersteds
Max. (BH) = 15,1 Megagauss × Oersteds (MG.Oe).

When the annealing operation is finished, the refractory stainless steel tube is quickly removed from the annealing furnace and suddenly quenched in water contained in a container in which stirring takes place.

The characteristics of the pieces so treated become:

density: 94 percent
Br = 7,900 Gauss
Hc = 7,000 Oersteds
Max. (BH) = 15,5 Megagauss × Oersteds (MG.Oe).

Water quenching has thus considerably improved the material's coercive field.

An attempt will be made below to explain why it has been possible to obtain the remarkable results mentioned above, though the value of the following theoretical explanation cannot have any effect on the value of the method, which rests solely on results obtained experimentally.

The alloy of the above mentioned composition theoretically has two phases Sm Co_5 and Sm_2 Co_7. However, as casting comprises sudden cooling, it is probable that these two phases coexist, but in an unco-ordinated way, at the time when thermal treatment begins.

The effect of pre-fritting would thus be to coordinate these two phases, the Sm_2 Co_7 phase surrounding the grains of Sm Co_5.

When fritting is done, the Sm_2 Co_7 phase is at a temperature close to its melting point, so that fritting is carried out with this material, which has a low melting point (and is thus in a pasty state) present at the grain boundaries, and is thus facilitated; the density is therefore improved. Moreover, the presence of Sm_2 Co_7 around Sm Co_5 prevents the evaporation of Sm and thus the formation of Sm_2 Co_{17}, the more so because the increase from the pre-fritting temperature to the fritting temperature, as well as the fritting operation itself, are fairly rapid.

Finally, the crystalline structure of the fritted product will be essentially the same as that of the Sm Co_5 alloy, the presence of Sm_2 Co_7 only constributing unco-ordinated defects. The result is that the saturation magnetization of the end product is very close to the ideal value defined by the Sm Co_5 structure.

In the temperature range in which annealing is carried out (around 900°C), the alloy is in the field where the Sm Co_5 is homogeneous and is therefore very anisotropic. On the other hand, if the material is then left to cool slowly, de-compounding occurs giving a mixture of phases: Sm Co_5 + Sm_2 Co_7 or Sm Co_5 + Sm_2 Co_{17}.

This de-compounding, which spoils the magnetic properties of the end product to a greater or lesser extent, is avoided by the sudden water quenching at this high temperature.

What is claimed is:

1. In a process of manufacturing a permanent magnet material based on samarium and cobalt, comprising the steps of: (a) preparing a powder of an alloy of samarium and cobalt, having a samarium content between 35 and 42 percent by weight and a cobalt content of between 65 and 58 percent by weight; (b) compacting the powder formed in step (a) under high pressure, while concurrently applying to the compact a magnetic field orienting the magnetic particles in the alloy; (c) sintering the compressed powder in an inert atmosphere; and (d) annealing the sintered compressed powder, the improvement comprising intermediate compacting step (b) and sintering step (c), the additional step of pre-fritting the compacted body of step (b) at a temperature of between 600° and 1000° C for a period of between 2 and 60 minutes to increase the density and residual induction properties of the final product.

2. Process according to claim **1**, wherein the sintering temperature is about 1,115° C and the sintering time is about 30 minutes.

3. Process according to claim **2**, wherein the pre-fritting temperature is about 750° C and the pre-fritting time is about 20 minutes.

4. Process according to claim **3**, wherein the samarium content in the alloy is about 37 percent by weight.

* * * * *