United States Patent [19]

Martin

[11] **3,892,598**

[45] **July 1, 1975**

[54] **COBALT-RARE EARTH MAGNETS COMPRISING SINTERED PRODUCTS BONDED WITH SOLID COBALT-RARE EARTH BONDING AGENTS**

[75] Inventor: **Donald L. Martin,** Elnora, N.Y.

[73] Assignee: **General Electric Company,** Schenectady, N.Y.

[22] Filed: **Jan. 7, 1974**

[21] Appl. No.: **431,126**

[52] **U.S. Cl.** **148/31.57;** 29/470; 148/103; 148/105; 264/56; 264/DIG. 58

[51] **Int. Cl.** **H01f 1/04**

[58] **Field of Search** ..... 148/31.57, 101, 103, 105; 29/472.7, 473.1, 470, DIG. 1; 264/56, DIG. 58; 65/43

[56] **References Cited**

UNITED STATES PATENTS

3,236,700	2/1966	Heimke et al.	148/31.57
3,239,323	3/1966	Folweiler	65/43
3,370,342	2/1968	Argyle et al.	29/472.7
3,655,463	4/1972	Benz	148/101

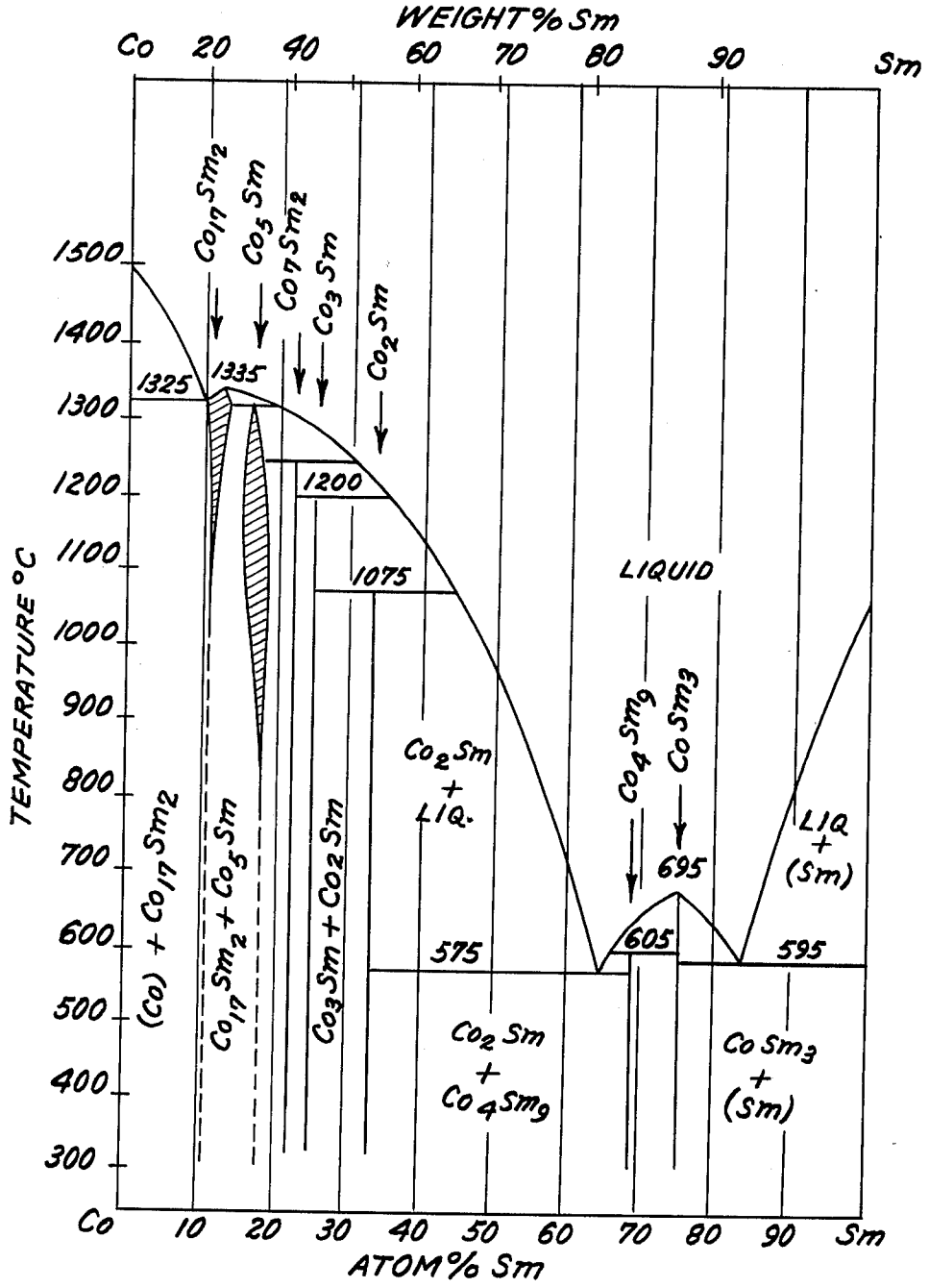
Primary Examiner—Walter R. Satterfield

Attorney, Agent, or Firm—Jane M. Binkowski; Joseph T. Cohen; Jerome C. Squillaro

[57] **ABSTRACT**

Permanent cobalt alloy magnets of large size are prepared. At least two compacts of particulate permanent magnet cobalt alloy are provided and a layer of particles of a bonding magnetic cobalt alloy agent is deposited on the bonding surface of one compact. The bonding surface of the second compact is contacted with the deposited bonding agent substantially coextensively therewith and the resulting assembly is sintered to produce a sintered bonded composite. The bonding agent is a solid at sintering temperature.

2 Claims, 1 Drawing Figure


WEIGHT% Sm
Co
20
40
60
70
80
90
Sm
$Co_{17}Sm_2$
Co_5Sm
Co_7Sm_2
Co_3Sm
Co_2Sm
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
1325
1335
1200
1075
LIQUID
Co_4Sm_9
$CoSm_3$
695
605
595
575
Co_2Sm + LIQ.
LIQ + (Sm)
Co_2Sm + Co_4Sm_9
$CoSm_3$ + (Sm)
(Co) + $Co_{17}Sm_2$
$Co_{17}Sm_2$ + Co_5Sm
Co_3Sm + Co_2Sm
TEMPERATURE °C
Co
10
20
30
40
50
60
70
80
90
Sm
ATOM% Sm

COBALT-RARE EARTH MAGNETS COMPRISING SINTERED PRODUCTS BONDED WITH SOLID COBALT-RARE EARTH BONDING AGENTS

The present invention relates to the art of cobalt-rare earth alloy permanent magnets and more particularly it relates to the art of bonding these magnets to produce magnets of desired large size or geometry without deleterious effect on magnetic properties.

Permanent magnets, i.e., "hard" magnetic materials, such as the cobalt-rare earth alloys, are of technological importance because they can maintain a high, constant magnetic flux in the absence of an exciting magnetic field or electrical current to bring about such a field.

Cobalt-rare earth intermetallic compounds or alloys exist in a variety of phases. Thus far, cobalt-rare earth alloys containing a substantial amount of Co_5R phase (in each occurrence R designates a rare earth metal) have exhibited the best magnetic properties. However, to produce a permanent magnet with satisfactory properties, the bulk Co-R alloy must be reduced to a powder which is then usually compressed in an aligning magnetic field to form an aligned pressed-powder compact. Specifically, the powder particles are magnetically aligned along their easy axis of magnetization prior to or during compaction since the greater their magnetic alignment, the better are the resulting magnetic properties.

The aligned pressed powder or green compact is sintered to produce a sintered body of the desired density. A magnetizing field is applied to the sintered body parallel to its easy axis of magnetization, generally at room temperature, to produce a permanent magnet.

A disadvantage of this technique is that the sintered body or magnet is limited by the size of the pressed-powder or green compact. The green compact, itself, is limited in size because of the high pressure required to press the powder into a compact with sufficient strength so that it can be handled without excessive breakage before sintering. Experience indicates that a minimum pressure of about 100,000 psi is needed. Thus, large magnets with an area greater than 4 to 5 square inches are difficult to make because of the need for pressure greater than 200 tons.

One way of making a large magnet piece is to join smaller magnets together. Unfortunately, a suitable joining or bonding medium has not been found. Low temperature bonding with solder or epoxy cement has been used to join cracked sintered pieces. The solder or epoxy bonding method while attractive for many applications, limits the use of such bonded magnets at elevated temperatures, particularly at temperatures in the range of 100°C to 200°C which deteriorate these bonding agents and weaken the bond significantly. Also, materials such as solder or epoxy cement are non-magnetic thereby introducing an air gap which dilutes the magnetic properties of the joined magnets somewhat.

The present process provides a method of bonding cobalt-rare earth alloy compacts without having any significant deleterious effect on the magnetic properties of the resulting bonded sintered magnet composite. Also, the bond in the composite is substantially as stable at elevated temperatures as the bonded sintered magnets. Specifically, the present bonding agent is a magnetic cobalt-rare earth alloy.

Those skilled in the art will gain a further and better understanding of the present invention from the detailed description set forth below, considered in conjunction with the figure accompanying and forming a part of the specification which is the cobalt-samarium phase diagram. It is assumed herein, that the phase diagram at 300°C., which is the lowest temperature shown in the figure, is substantially the same at room temperatures.

Briefly stated, the present process comprises providing at least two compacts to be bonded together and sintered at a sintering temperature ranging from 900°C to 1250°C. Each compact consists essentially of compacted particulate permanent magnet alloy selected from the group consisting of Co-R, (Co-Fe)R, (Co-Cu)R, and (Co-Fe-Cu)R, where R is a rare earth metal. A layer of particles of a bonding magnetic alloy agent is deposited on the bonding surface of one of the compacts, said agent being selected from the group consisting of Co-R, (Co-Fe)R, (Co-Cu)R, and (Co-Fe-Cu)R, where R is a rare earth metal. The bonding agent is a solid at sintering temperature and contains the rare earth metal component in a minimum amount of at least 0.1 atom % higher than that contained in the compacts being bonded. The bonding surface of the second compact is contacted with the deposited bonding agent substantially coextensively therewith, and the resulting assembly is sintered at a sintering temperature ranging from 900°C to 1250°C in an atmosphere in which it is substantially inert to bond and sinter said assembly to produce a solid composite sintered product having a density of at least 87%.

The rare earth metals useful in forming the present bonding agents and the permanent magnet alloy or alloys of the present compacts are the 15 elements of the lanthanide series having atomic numbers 57 to 71 inclusive. The element yttrium (atomic number 39) is commonly included in this group of metals and, in this specification, is considered a rare earth metal. A plurality of rare earth metals can also be used to form the present cobalt-rare earth alloys which, for example may be ternary, quartenary or which may contain an even greater number of rare earth metals as desired.

Representative of the cobalt-rare earth alloys useful in the present invention are cobalt-cerium, cobalt-praseodymium, cobalt-neodymium, cobalt-promethium, cobalt-samarium, cobalt-europium, cobalt-gadolinium, cobalt-terbium, cobalt-dysprosium, cobalt-holmium, cobalt-erbium, cobalt-thulium, cobalt-ytterbium, cobalt-lutecium, cobalt-yttrium, cobalt-lanthanum and cobalt-mischmetal. Mischmetal is the most common alloy of the rare earth metals which contains the metals in the approximate ratio in which they occur in their most common naturally occurring ores. Examples of specific ternary alloys include cobalt-samarium-mischmetal, cobalt-cerium-praseodymium, cobalt-yttrium-praseodymium, and cobalt-praseodymium-mischmetal.

In the present process at least two compacts are provided which are to be bonded together and sintered at a sintering temperature ranging from 900°C to 1250°C. Each compact consists essentially of compacted particulate permanent magnet alloy selected from the group consisting of Co-R, (Co-Fe)R, (Co-Cu)R, and (Co-Fe-Cu)R, where R is a rare earth metal or metals. The permanent magnet alloy can be formed by a number of conventional methods and converted to particulate

form in a conventional manner. Its particle size may vary and it can be in as finely divided a form as desired. For most applications, average particle size will vary from about 1 micron or less to about 10 microns. Larger sized particles can be used but the maximum intrinsic coercive force obtainable is lower because it decreases with increasing particle size. The powder particles are magnetically aligned along their easy or preferred axis of magnetization prior to or during compression since the greater the magnetic alignment, the better are the resulting magnetic properties. The aligned powder is pressed to a compact of desired size and shape. Compression can be carried out by a number of conventional techniques such as hydrostatic pressing or methods employing steel dies. The density of the aligned compacts generally ranges from about 70 to 80% of theoretical.

The present bonding agent is a solid at room temperature and at elevated temperature ranging up to and including sintering temperature, and it is an alloy selected from the group consisting of Co-R, (Co-Fe)R, (Co-Cu)R, and (Co-Fe-Cu)R, where R is a rare earth metal or metals. The agent can vary in composition which can be determined from the phase diagram for the particular system or which can be determined empirically. For example, the accompanying figure shows that for the Co-Sm system, at a sintering temperature of 1100°C, the solid bonding agent can obtain samarium in a maximum amount of about 42 atom %. The present bonding agent is one which is at least 0.1 atom %, and preferably at least 5 atom %, richer in rare earth metal content than that of the compacts being bonded. This richer rare earth metal content is necessary to attain adequate adhesion of the agent to the bonding surfaces of the magnets in order that a strong bond be formed. The bonding agent need not be composed of the same components as those of the alloys in the compacts being bonded. For example, a Co-Sm alloy bonding agent can be used to bond compacts composed of Co-Fe-Cu-Sm-Pr alloy. The maximum amount of rare earth component in the present solid bonding agent is about 55 atom % with the particular maximum amount depending on the particular bonding agent composition and the particular results desired.

The bonding surfaces of the compacts are not even or level surface but have a roughness corresponding to the projections of the compacted particles. Although the particle size of the bonding agent can vary, it is preferably very fine in size so that when it is deposited on the uneven bonding surface of the compact, it will contact bonding surface between projections and thereby be in contact with a larger bonding surface area resulting in a stronger bond being formed during sintering. Specifically, since the particles in the compact generally range from about 1 micron to 10 microns in size, the present bonding agent also preferably will range from about 1 micron to 10 microns in size. A bonding agent having a particle size significantly higher than 10 microns will not contact sufficient area of the bonding surface during sintering to produce a suitable bond. Specifically, the particles of bonding agent should be in contact with at least 50% of the surface area being bonded.

In carrying out the process of the present invention, a layer of the bonding alloy agent particles is deposited on a surface of one of the aligned compacts to be bonded. Since the aligned compact is somewhat magnetic, the deposited particles cling to its surface. The particular amount of the bonding agent deposited should be sufficient to result in a good bond in the sintered composite product and is determinable empirically. Preferably, the bonding agent is deposited to form a continuous layer or deposit on the bonding surface. The surface of the second compact to be bonded is then placed in contact with the deposited layer substantially coextensively therewith.

The resulting assembly is heated to sintering temperature in an atmosphere in which it is substantially inert. Frequently, the aligned compacts are sufficiently magnetic so that the assembly holds together, if maintained vertically, until the Curie temperature is reached and then just the weight of one compact on top of the other will hold it together during sintering. However, if desired, the assembly can be supported or held together by conventional means such as a clamp.

The assembly is sintered in a substantially inert atmosphere to produce a solid sintered composite wherein the pores are substantially non-interconnecting, which generally is a sintered composite having a density of at least about 87% of theoretical. Such non-interconnectivity stabilizes the permanent magnet properties of the composite product because its interior is protected against exposure to the ambient atmosphere.

The present permanent magnet type cobalt alloy systems require a sintering temperature ranging from 900°C to 1250°C. The particular sintering temperature depends largely on the particular cobalt alloy system being sintered. For example, for Co_5Sm type alloys a sintering temperature of 1120°C is particularly satisfactory.

The sintered composite is cooled, preferably, in an atmosphere in which it is substantially inert, preferably to room temperature. A magnetizing field is applied to the sintered composite along its easy axis of magnetization, preferably at room temperature, to produce a permanent magnet.

The density of the sintered composite may vary. The particular density depends largely on the particular permanent magnet properties desired. In the present invention, the density of the sintered composite ranges from about 87 to 100% of theoretical.

Specifically, magnet composition and sintering techniques particularly useful in the present invention are disclosed in U.S. Pat. Nos. 3,655,464; 3,655,463; and 3,695,945, all filed in the name of Mark G. Benz, and assigned to the assignee hereof, and all of which by reference are made part of the disclosure of the present application. Each of the aforementioned patents discloses a process for preparing novel sintered cobalt-rare earth intermetallic products which can be magnetized to form permanent magnets having stable improved magnetc properties.

The solid composite of the present invention has a bond or joint which is visible to the naked eye. This bond is magnetic so that it does not diminish the properties of the bonded magnets of any significant extent. Also, this bond is heat-stable, i.e., it is not significantly affected at the elevated temperatures at which the bonded magnets must be operable. Specifically, it is substantially as heat-stable as the bonded magnets, themselves.

If desired, a layer of particles of bonding alloy agent can be deposited on the bonding surface of each of a number of compacts which can be stacked up, one

upon the other, coextensively with each other and sintered, to form the desired bonded sintered composite structure.

The present invention is useful for preparing large and/or complex permanent magnet structures for such diverse applications as meters and instruments, magnetic separators, computers and microwave devices.

The invention is further illustrated by the following example.

EXAMPLE

Particles of a 66.7 wt.% cobalt-33.3 wt.% samarium base alloy were admixed with particles of an additive 40 wt.% cobalt-60 wt.% samarium alloy to form a thorough mixture composed of 63 wt.% cobalt and 37 wt.% samarium. The particles had an average size of about 6 microns.

A portion of the mixture was magnetically aligned along the easy axis by an aligning magnetizing field of 60 kiloersteds. After magnetic alignment, it was pressed to form a compact which was in the shape of a bar about one inch long and about ⅛ inch in diameter and had a packing of about 80 percent. This sample, which was the control sample, was sintered in an atmosphere of argon at a temperature of 1120°C for one hour, furnace-cooled to 875°C where it was heat-aged for 5 hours and then cooled to room temperature in the same atmosphere.

Two additional portions of the mixture were aligned and compacted in a substantially the same manner as the control sample to form two compacts, each of which were in the shape of a bar about ½ inch long and ⅓ inch in diameter and having a packing of about 80 percent. The bonding surface of one of these compacts, i.e., the surface across the width thereof, was plunged into particles of a bonding alloy agent, and when it was removed therefrom, it had a substantially continuous layer of bonding agent particles clinging thereto.

The bonding alloy agent was composed of 59 wt.% cobalt-41 wt.% samarium and had a particle size of about 10 microns. All of this bonding agent was a solid at room temperature as well as at elevated temperatures including sintering temperature, and it was about 4 atomic % richer in samarium than the samarium content of the compacts being bonded. The bonding surface of the second compact was contacted with the deposited bonding alloy agent substantially coextensively therewith to form an assembly in the form of a bar about one inch long. The assembly was sintered at a temperature of 1120°C for one hour, then furnace-cooled to a temperature of 875°C where it was heat-aged for five hours and then cooled to room temperature in the same atmosphere. The bonded portion of the resulting composite appeared as an uneven thin line. The bonded portion of the composite appeared to be strong and did not break when force was applied manually.

A magnetizing field of 60 kiloersteds was applied at room temperature along the easy axis of magnetization to the control sample as well as the bonded composite and their magnetic properties were determined as shown in the following table where:

B_s is the saturation induction.

B_r is the residual or remanent induction, i.e., the flux when the applied magnetic field is reduced to zero.

Normal coercive force H_c is the field strength at which the induction B becomes zero.

The term H_k helps characterize the squareness of the $4\pi M$ demagnetization curve. Specifically, H_k is the demagnetizing field required to drop the magnetization 10 percent below the remanence B_r. That is, $4\pi M_k = .9\ B_r$, and H_k is the corresponding field strength. H_k is a useful parameter for evaluating demagnetization resistance.

The intrinsic coercive force H_{ci} is the field strength at which the magnetization (B–H) or $4\pi M$ is zero.

The maximum energy product $(BH)_{max}$ represents the maximum product of the magnetic field H and the induction B determined on the demagnetization curve.

TABLE

Sample	B_s gauss	B_r gauss	H_c oers.	H_k oers.	H_{ci} oers.	$(BH)_{max}$ (10^6gauss oers.)	Density %	Alignment
Control Sample - Sample Sintered Piece	9,740	8,970	8,900	23,300	29,500	19.8	94.2	.977
Bonded Sintered Composite	9,790	9,160	9,000	21,500	28,100	20.7	95.1	.984

As shown by the table, the present bonded composite has magnetic properties which are substantially the same as those of the control sample. This illustrates that the present bonding agent has no significant effect on the magnetic properties of the bonded magnets.

The control sample and the bonded composite were then placed in an air oven maintained at 260°C for about 24 hours and then cooled to room temperature in air. Force applied manually to the bonded portion of the composite indicated that heating in air at this elevated temperature did not weaken the bond.

In copending U.S. Pat. application Ser. No. 431,127 entitled "Bonding Agent for Cobalt-Rare Earth Alloy Magnets and Composite" filed on even date herewith in the name of Donald L. Martin and assigned to the assignee hereof, and which by reference is made part of the disclosure of the present application, there is disclosed a process for producing sintered permanent magnets of large size. Briefly, the process comprises providing at least two compacts of particulate permanent magnet alloy, depositing a layer of particles of a bonding magnetic cobalt alloy agent on the bonding surface of one compact, contacting the bonding surface of the second compact with the deposited bonding agent substantially coextensively therewith, and sintering the resulting assembly to produce a sintered bonded composite. At least 1% by volume of the bonding agent passes through a liquid phase at an elevated temperature.

What is claimed is:

1. A cobalt-rare earth alloy permanent magnet having an area greater than 4 square inches and substantially uniform permanent magnet properties throughout, said magnet consisting essentially of a sintered

product consisting essentially of at least two compacts bonded together by a magnetic bonding agent, each said compact being produced by providing a permanent magnet type alloy of cobalt and rare earth metal in particulate form having an average particle size up to about 10 microns, subjecting said particulate alloy to a magnetic field to align the particles along their easy axis of magnetization, and compressing said particulate alloy into a compact having a density of at least 70%, said sintered product being produced by depositing a layer of particles ranging in size up to 10 microns of a magnetic bonding agent on the bonding surface of one of said compacts substantially covering said surface with said agent, said agent being a solid at sintering temperature and consisting essentially of cobalt-rare earth alloy containing the rare earth component in an amount at least 5 atom % greater than that of the alloy of each said compact with the maximum amount of rare earth component being 55 atom %, contacting the bonding surface of the second compact with said deposited bonding agent substantially coextensively therewith, and sintering and bonding the resulting assembly at a temperature ranging from 900°C to 1250°C in an atmosphere in which it is substantially inert producing a solid sintered composite product having a density of at least 87%.

2. A permanent magnet according to claim 1 where R is samarium.

* * * * *