

[54] **POWDERIZED COBALT RARE EARTH
METAL COMPOUNDS AND PROCESS FOR
MAKING SUCH COMPOUNDS**

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75/.5 BA, 152; 148/101, 105, 103, 31.57;
23/294; 241/18, 22, 184, 176

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[57]

ABSTRACT

Powderized compounds of cobalt and one or more rare earth metals are produced in a gas transport reaction whereby the reaction components are kept in motion at least in a zone where the compounds accumulate and whereby said reaction components are simultaneously subjected to the action of grinding or milling weights.

5 Claims, 2 Drawing Figures

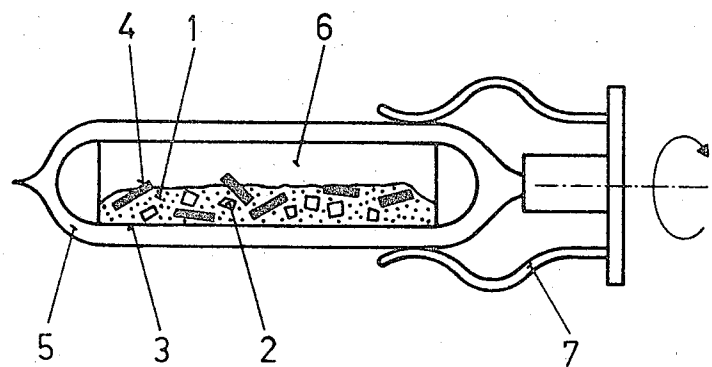


Fig. 1

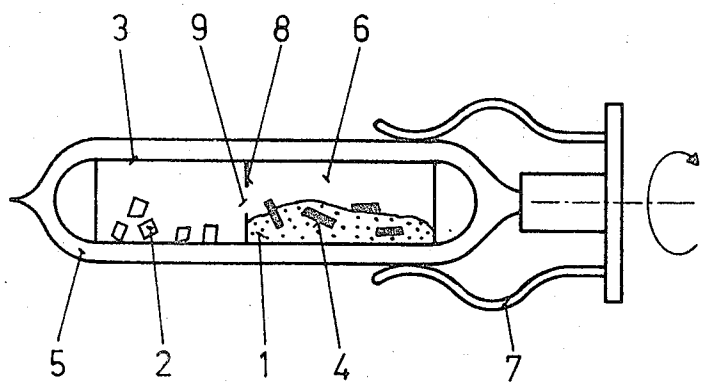


Fig. 2

POWDERIZED COBALT RARE EARTH METAL COMPOUNDS AND PROCESS FOR MAKING SUCH COMPOUNDS

BACKGROUND OF THE INVENTION

The invention relates to a process for the preparation of pulverulent or powdered compounds of cobalt and any rare earth metal or mixtures of such rare earth metals, whereby a gas transport reaction is employed. The present powdered compounds are especially useful for making hard magnets.

Pulverulent compounds made of cobalt and rare earth metals or mixtures thereof have achieved great importance for the production of permanent magnets, because they have a very high coercive force (see, for example, "Scientific American", December 1970, pages 92 et seq or "Physik In Unserer Zeit", 1970, No. 4, pages 103 et seq).

In the known processes for the production of pulverulent compounds, the compound is first produced by metallurgical melting processes and then the resulting product is ground. For producing a magnet, the powder is then usually screened, brought into an aligning magnetic field, pressed into a blank and finally sintered.

The disadvantage of the known processes is seen in that the outstanding magnetic properties of the powder are greatly impaired during the sintering process. The reason for this is generally thought to be that considerable impurities, and particularly oxygen, are incorporated into the regions of the powder grains near the surface, during the grinding process. This occurs even if the grinding process is carried out in an inert gas atmosphere, for example, helium or argon, or under a protective liquid for example xylene.

To obviate this disadvantage, it is known (D. L. Martin, M. G. Benz, G. E. Report No. 70-C-261) to add a sintering aid to the powder to be sintered in the form of a pulverulent additive which is liquid at sintering temperature. The effect of this additive is not completely known. In addition to the formation of the liquid phase, the binding of the detrimental oxygen by the additive would appear to be rather important. Without the sintering aid, the oxide Sm_2O_3 forms in the case of Co-Sm so that the required Co_5Sm phase passes partially over to $\text{Co}_{17}\text{Sm}_2$ which, however, has a poor coercive force.

To avoid the expensive grinding process, it has been proposed to make the powder directly from the elements by a gas transport reaction, wherein the reaction mixture is kept locally in motion more particularly the mixture is rotated in order to obtain better mixing. With this process, however, the coercive forces obtained with the powder are not quite equivalent to the values obtained when mechanical grinding is employed. This may be due to the fact that Bloch wall keying points produced by the mechanical grinding process are absent in the above gas transport reaction process, or that the resulting grains are too large.

OBJECTS OF THE INVENTION

In view of the above it is the aim of the invention to achieve the following objects singly or in combination:

to overcome the drawbacks of the prior art, more specifically to produce improved cobalt rare earth metal compounds while employing the gas transport reaction;

to produce cobalt rare earth metal powders having high coercive forces and which are thus rather suitable for further processing to form fine-particle hard magnet;

to produce cobalt rare earth metal compounds in powdered form having an average grain size from about 1μ to about 5μ ; and

to produce a cobalt rare earth metal compound in powdered form having, when formed into a magnet coercive forces in excess of 20,000 Oersted.

SUMMARY OF THE INVENTION

To this end, according to the invention, in the process described above, the reaction components are kept in motion and simultaneously subjected to the action of grinding weights.

According to a preferred embodiment of the invention, the gas transport reaction may take place in such a manner that the reaction components are heated in a closed reaction system or space into which the reaction components have been introduced in their solid state form in the presence of a transport substance, especially iodine. The reaction components and the transport substance form compounds which are volatile at the reaction temperature whereby the equilibrium constant of the reaction system is such that a reaction between the volatile cobalt compound and a rare earth metal is possible whereby cobalt is released and that further a reaction is possible between the volatile rare earth metal compound and cobalt whereby the rare earth metal is released.

The gas transport reaction may also be accomplished according to a modified embodiment wherein the cobalt in powder form and the rare earth metal or mixtures of rare earth metals in any suitable form, for example in coarsely comminuted form, are heated in a common reaction chamber to a temperature at which the rare earth metal or the rare earth metal mixtures evaporate to a substantial extent and at which temperature the cobalt vaporizes merely insignificantly.

In both types of reaction the compound which is thermodynamically most stable under the selected stoichiometry and the selected reaction temperature is obtained after a suitably long reaction time has expired and after intermediate phases have been formed.

BRIEF FIGURE DESCRIPTION

In order that the invention may be clearly understood, it will now be described, by way of example, with reference to the accompanying drawings, wherein:

FIG. 1 shows an apparatus for performing the process according to the invention, in which a special transport substance is provided, and

FIG. 2 is an apparatus for performing the process according to the invention without a special transport substance.

DETAILED DESCRIPTION OF EXAMPLE EMBODIMENTS

Example 1

It is the aim of the invention to produce a cobalt samarium compound of the formula Co_5Sm by employing a gas transport reaction and using a special transport substance.

To this end referring to FIG. 1, 11.76 g of cobalt 1 and 7.20 g of samarium 2 in the form of lumps, shavings

or powder were weighed and placed in a tantalum ampoule 3 having a length of 100 mm and a diameter of 20 mm equivalent to a volume of 31.5 cc. 0.22 g of iodine (not shown) was added as a gas transport agent. The excess of samarium above the stoichiometric ratio of 5:1 of the end product Co_5Sm was about 20 percent in order to bind the iodides to be precipitated at the end of the reaction and in order to compensate for entrained oxygen-containing impurities in the starting materials and for reactions with the vessel wall.

Grinding weights 4 of molybdenum, tungsten or tantalum were also introduced, for example 90 g of molybdenum pins of a diameter of 1 mm and a length of 5 mm.

The tantalum ampoule 3 was then vacuum sealed and fused under vacuum into a quartz ampoule 5. The latter was rotated by a device 7 in an oven (not shown) at a temperature of between 750°C and $1,150^\circ\text{C}$, e.g., 850°C , and at about 10 to 500, e.g. 100 r.p.m. The reaction to Co_5Sm by isothermal gas transport takes place under these conditions, partly by way of thermodynamically unstable intermediate phases. The lower the selected reaction temperature is the more time will the reaction require. This fact and the material with which the reaction components, especially the iodine, come into contact (vessel walls, grinding weights) determine the above-mentioned lower temperature limit. Nevertheless, such lower limit is not critical. The reaction is carried out for a period ranging from a few hours to several days, for example 24 hours, and then the ampoule is cooled and opened in ethanol. After washing out the iodides (mainly SmI_3), Co_5Sm powder is obtained with a coercive force of $H_c > 20,000$ Oe. This high coercive force is caused by the grinding weights. Without the latter, the resulting product has a coercive force of only $H_c \approx 5,000$ Oe. There is as yet no explanation for this surprising effect of the grinding weights. It would appear that the fact that the powder grains are kept small, approximately $1-5\mu$ diameter as compared to $20-100\mu$ diameter without grinding weights, due to the avoidance of primary sintering plays some part. Probably, however, suitable lattice defects are introduced by plastic deformations which serve as anchoring sites for the Bloch walls whereby magnetic reversal is made more difficult.

In order to vary the pressure reaction parameter, an inert gas may be provided in the reaction chamber 6, which is small in order to reduce the transport distances. The temperature reaction parameter can be varied locally and/or as a function of time within the thermodynamic limits determined by the end product.

Example 2

This relates to the production of high-coercivity Co_5Sm by gas transport reaction without the use of a special transport substance.

To this end, referring to FIG. 2, 29.47 g of cobalt powder 1 and 15.035 g of samarium shavings 2 and balls or pins 4 of molybdenum, tungsten, or tantalum having a diameter of about 1-5 mm and a total weight of 250 g were introduced into a tantalum reaction vessel 3 which was vacuum sealed and fused under vacuum into a quartz ampoule 5.

The ampoule 5 was then secured to the device 7 whereby the ampoule can be rotated about the longitudinal axis. The ampoule and its rotating device were

placed into an oven (not shown). The oven was heated to $750^\circ - 1,150^\circ\text{C}$, e.g., 850°C , and the quartz ampoule 5 together with the reaction vessel 3 and contents was left therein for a period ranging from a few hours to several days, for example 24 hours. The ampoule was rotated at about 10-500, e.g., 100 r.p.m. As in example 1, here again the temperature limits are not critical.

The reaction chamber 6 is divided into two chambers by a partition 8 having an opening 9. The samarium shavings 2 are disposed in one chamber and the cobalt powder 1 and grinding weights 4 in the other chamber. Reaction components 1, 2 and the grinding weights 4 may alternatively be used as shown in FIG. 1 in a mixture with one another and located in a reaction chamber without a partition.

During heating and simultaneous rotation in the oven, the samarium diffuses as a vapor through the opening 9 in the apparatus shown in FIG. 2 to the cobalt powder 1 where it reacts with the cobalt. Cobalt has a vapor pressure of about 10^{-9} Torr at a temperature of 850°C , while samarium has a vapor pressure of about 2×10^{-1} Torr at the same temperature. There is therefore migration of practically only the samarium.

During the reaction between the samarium and the cobalt, intermediate phases of different stoichiometry are being formed, for example $\text{Sm}_2\text{Co}_{17}$, Sm_2Co_7 and the like, the melting point of which is, however, greater than the maximum reaction temperature of $1,150^\circ\text{C}$. The intermediate phases finally dissolve in favor of the thermodynamically most stable end phase SmCo_5 .

As in example 1, the effect of the rotary movement with the molybdenum pieces 6 is that the reaction mixture is thoroughly mixed and does not sinter together. At the same time, a particular effect is that the reaction product is magnetically hardened and has a very high coercive force at the end of the reaction.

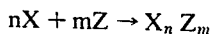
The reaction is complete after a period ranging from a few hours to several days, depending upon the temperature. For example, completion after 24 hours is accomplished at 850°C , whereby Co_5Sm is obtained in powder form which is removed from the vessel after cooling.

The shape and particle size of the finished product are dependent upon the following parameters: the reaction temperature, reaction time, size and shape of the molybdenum grinding pieces, and the ratio of the weight of the charge ($\text{Sm} + 5\text{Co}$) to the total weight of molybdenum pieces. A desired particle size and particle shape for the reaction product can be obtained by suitable selection of the parameters within certain limits.

The shape and size of the powder to be produced can also be influenced by different temperatures in the sub-chambers of the reaction vessel 3. If the temperature in the chamber containing the samarium 2 is too high, a eutectic may form in the Co powder 1, this is undesirable because it has too low a melting point since the samarium vaporizes too rapidly and the supply in the chamber containing the cobalt is correspondingly high. The molten eutectic may then bond the grains so strongly that the molybdenum pieces 6 cannot break open the layer whereby the further reaction is stopped. The lower the temperature in the chamber containing the cobalt powder 1, the slower the diffusion of samarium into the cobalt grains and hence the slower the reaction to the end product. The coercive force of the

SmCo₅ can also be influenced or optimized by suitable selection of the temperatures in the two chambers.

The process described in this example is always applicable if one of the components, for example X or Sm in the reaction:



for example



has a much higher vapor pressure than the other component, i.e., Z or Co, and if the intermediate phases e.g., Sm₂Co₁₇ and the like, have melting points higher than the lowest reaction temperature still practical in the chamber of the reaction vessel 3 containing the cobalt powder 1 in FIG. 2.

The process according to the invention can also be used to great advantage for the preparation of other cobalt and rare earth metal compounds, for example CeMM_{0.5}Sm_{0.5}Co₅, wherein MM denotes the "misch metal" which is well known in the steel production as a mixture of rare earth metals.

Although the invention has been described with reference to specific examples, it is to be understood, that it is intended to cover all modifications and equivalents within the scope of the appended claims.

What is claimed is:

1. In a process for producing powdered SmCo₅ from a mixture of reaction components of cobalt and samarium

by a gas transport reaction in a reaction vessel; the improvement comprising introducing into said reaction vessel as a reaction material powdered cobalt having a grain size of up to 100μ and samarium comminuted to pieces of up to and including millimeter size, whereby the proportions of samarium and cobalt are such that the stoichiometric ratio of 5:1 in the end product SmCo₅ is assured, introducing grinding weights of suitable size into said reaction vessel, said grinding weights being of a material selected from the group consisting of W, Mo and Ta, evacuating and sealing the reaction vessel, keeping said reaction vessel in motion for a period of from a few hours to several days while simultaneously heating the reaction material and grinding weights to a temperature within the range of about 750° to 1150°C, and then cooling and opening said reaction vessel to obtain said powdered SmCo₅.

2. The process of claim 1, further comprising adding to said reaction components a quantity of iodine.

3. The process of claim 1, comprising providing an excess of about 10 to 20 percent of samarium above the samarium required to satisfy said stoichiometric ratio.

4. The process of claim 1, wherein said keeping of the reaction vessel in motion is accomplished by rotating the reaction vessel at an rpm of about 10 to 500.

5. A samarium cobalt-powder product when produced according to the process of claim 1.

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