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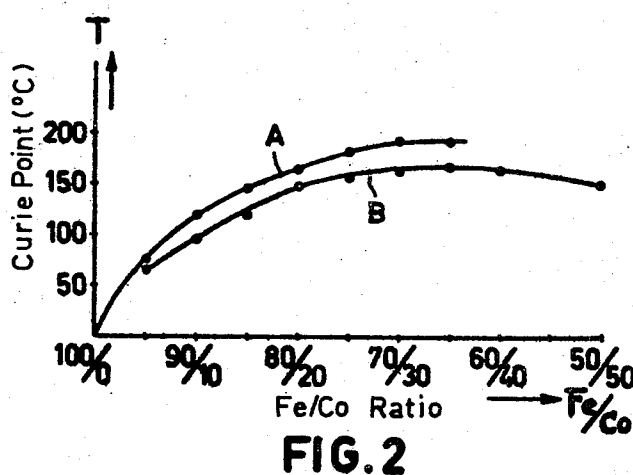
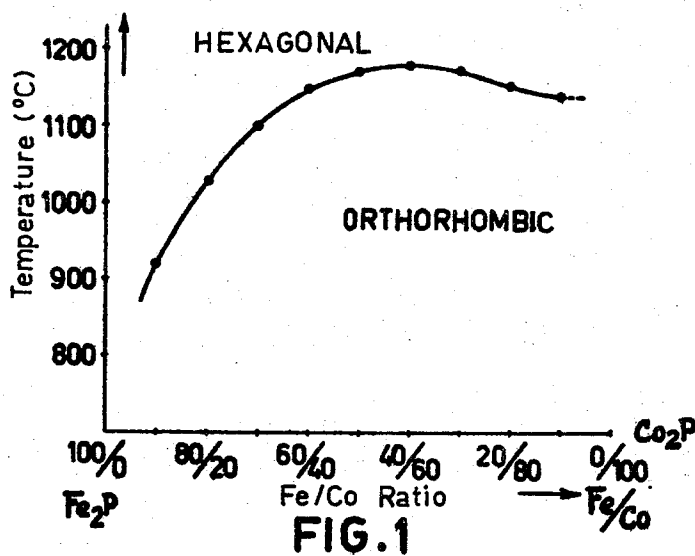
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3,188,247

USE OF THE HEXAGONAL PHASE OF THE COMPOUND $(\text{Fe}, \text{Co})_2\text{P}$ IN
PARTICLE SIZE PERMANENT MAGNETS

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2 Sheets-Sheet 1



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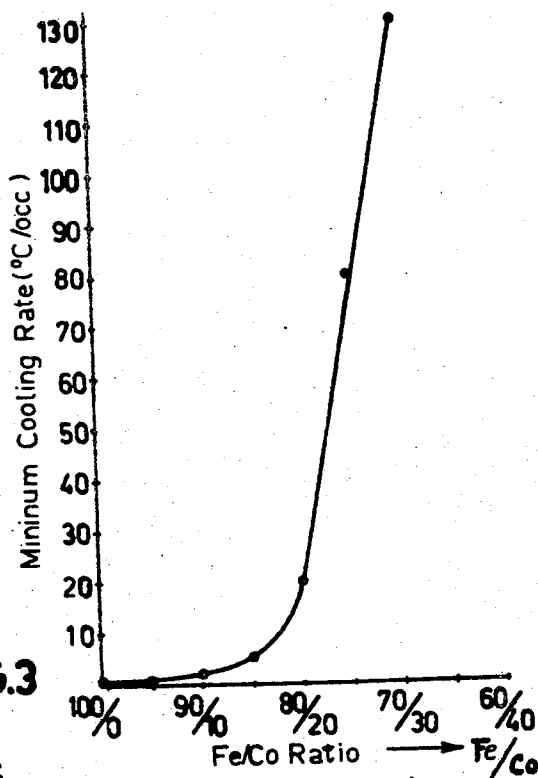


FIG. 3

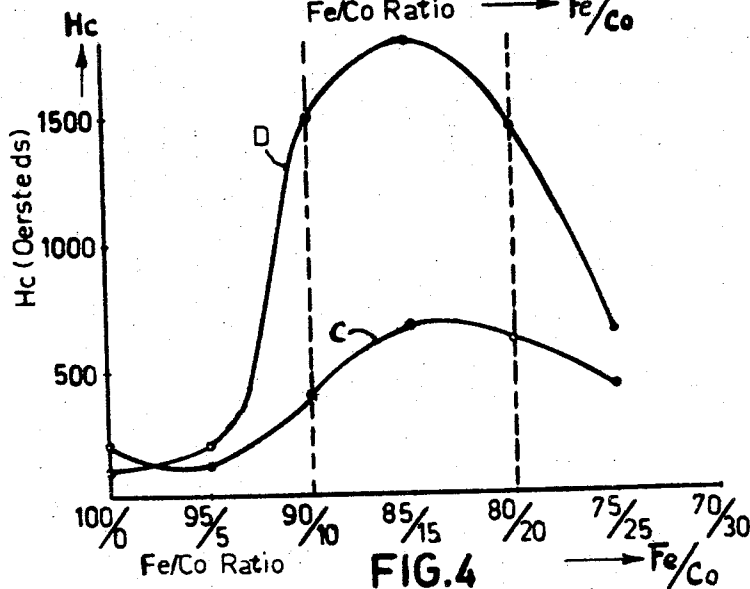


FIG. 4

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Our invention relates to the manufacture of permanent magnets formed of particle-size permanent magnets in which the constituent essential for obtaining permanent magnetic properties is the hexagonal phase of the compound $(\text{Fe},\text{Co})_2\text{P}$.

Permanent magnets of the above type have been described in U.S. patent application Ser. No. 131,326 filed August 14, 1961, which states that the $(\text{Fe},\text{Co})_2\text{P}$ -particles with an Fe/Co ratio up to 80:20 may be fully in one phase with the hexagonal Fe_2P -structure at room temperature. This application further states that the $(\text{Fe},\text{Co})_2\text{P}$ -particles having an Fe/Co ratio of less than 80:20, particularly $(\text{Fe},\text{Co})_2\text{P}$ -particles having an Fe/Co ratio up to 60:40, may still contain the hexagonal phase and thus are suitable for the manufacture of permanent magnets.

We have found that the permanent magnetic properties and Curie point of such magnets are deleteriously affected by the formation at the lower temperatures of the orthorhombic phase and, in accordance with the invention, these difficulties are overcome by means of a rapid cooling of the particles at rates which depend upon the cobalt content and over temperature ranges whose upper limit depends upon the Fe/Co ratio, to thereby suppress the formation of such a phase.

In order that our invention may be clearly understood and readily put into effect we shall describe the same in more detail in reference to several specific examples and to the accompanying drawing which:

FIGURE 1 is a constitutional diagram of the quasi-binary section $\text{Fe}_2\text{P}-\text{Co}_2\text{P}$.

FIG. 2 is a diagram showing Curie points of various alloys with the hexagonal and orthorhombic phases.

FIG. 3 is a graph showing for various alloys minimum cooling rates according to the invention, and

FIG. 4 is a graph showing the coercive force at room temperature of $(\text{Fe},\text{Co})_2\text{P}$ particles made by our method before and after heating.

From FIGURE 1, which was obtained by differential thermo-analysis and X-ray examination, it is seen that the hexagonal phase in the quasi-binary section between Fe_2P and Co_2P of the ternary constitutional diagram Fe-Co-P probably extends, at high temperature, as far as compound Co_2P itself. FIGURE 1 also shows that the hexagonal phase of $(\text{Fe},\text{Co})_2\text{P}$, which is stable at the higher temperatures, passes at lower temperatures into another phase which can be described as the orthorhombic phase, and that the transition temperature varies with the composition.

As shown in FIGURE 2, in which curve A represents the hexagonal phase and curve B represents the orthorhombic phase it is seen that the orthorhombic phase, which is also ferromagnetic, has a Curie point which is lower than that of the hexagonal phase. We have found that the presence at room temperature of this orthorhombic phase with the hexagonal phase adversely affects the permanent magnetic properties of the ferromagnetic particles, especially reduces the coercive force which in turn reduces the BH_{max} value.

We have also found that the undesirable conversion of the hexagonal phase, which is stable at high temperatures,

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into the orthorhombic phase existing at a low temperature takes place at a higher rate according as the cobalt content of the particles increases, i.e., as the iron-cobalt ratio decreases.

According to the method of our invention $(\text{Fe},\text{Co})_2\text{P}$ -particles having an Fe/Co ratio of between 90:10 and 60:40 are brought substantially completely into the hexagonal phase at room temperature by cooling the particles through a temperature range having an upper limit which lies between about 900° C. and about 1150° C., and increases as the Fe/Co ratio decreases and a lower limit below about 600° C. The cooling is carried out at an average rate which varies with the cobalt content and increases according as the cobalt content increases, with the understanding that for alloys having a Fe/Co ratio of 90:10, the cooling rate must be at least about 2° C./sec. and for the alloys having a Fe/Co ratio of between 75:25 and 60:40, this ratio should exceed about 75° C./sec.

FIGURE 3 shows the minimum average cooling rates between about 1200° C. and about 600° C. for the various alloys as a function of the Fe/Co ratio.

So far we have not succeeded in quenching $(\text{Fe},\text{Co})_2\text{P}$ -alloys having an Fe/Co ratio of less than 60:40 so rapidly that, at room temperature, they consist substantially completely of the hexagonal phase.

The coercive force of the $(\text{Fe},\text{Co})_2\text{P}$ -particles cooled down in the manner of our invention may be even further increased by heating the particles in a non-oxidizing atmosphere at a temperature preferably lying below 650° C. for a period of time which increases as the temperature lies further below 650° C. For reasons of diffusion velocity, the lowest heating temperature should not be less than about 300° C. These heat-treatments are effected in the range in which the orthorhombic phase is stable. Therefore, when the heat-treatment is of too long duration, the orthorhombic phase occurs again beside the hexagonal phase, as a result of which the coercive force may decrease again. If a heating temperature higher than 650° C. is used this results in a decrease of the coercive force even with heat-treatments of very short duration. Therefore, the highest heating temperature should preferably not exceed 650° C.

We have found that, as shown between the broken lines in FIG. 4, a maximum occurs in the coercive force, particularly for the particles having Fe/Co ratio of between 90:10 and 80:20, both after cooling from the range of the hexagonal phase and after the heat-treatment at a temperature lying between 650° C. and 300° C. The maximum increase of the coercive force is obtained if the $(\text{Fe},\text{Co})_2\text{P}$ -particles, after having been cooled down, are heated in a temperature range between about 400° C. and 500° C. Referring to FIG. 4, curve C shows the coercive force at room temperature for $(\text{Fe},\text{Co})_2\text{P}$ -particles immediately after they have been cooled down from a high temperature at a rate of approximately 100° C./sec., and curve D shows the coercive force of such particles after being subjected to heat-treatment at a temperature lying between 400° C. and 500° C.

The $(\text{Fe},\text{Co})_2\text{P}$ -particles may be compressed, if desired, in a magnetic field, to form a composite magnet body. It has been found that the coercive force of the particles is adversely affected by stress in general and consequently also by the compression. This decrease of the coercive force of the particles which have been subjected to stress may be wholly or partly eliminated by subjecting the particles again to a heat-treatment in the temperature range lying below 650° C., as described hereinbefore. It is not necessary for the cooled $(\text{Fe},\text{Co})_2\text{P}$ -particles to be previously heated in the temperature range lying between 650° C. and 300° C. and then compressed, for example, to form a magnet body and finally heated again in the said temperature range, but the particles may be com-

pressed, if desired in a magnetic field, to form a magnet body immediately after being cooled down and subsequently heated in the temperature range lying between 650° C. and 300° C. The coercive force in this case also increases to a value which differs only slightly from that of the particles treated in accordance with the first-mentioned method.

Example 1

A melt was formed of 95% by weight of phosphorus-copper, 4.25% by weight of iron and 0.75% by weight of cobalt containing $(\text{Fe,Co})_2\text{P}$ -particles having a Fe/Co ratio of 85:15. This melt was cooled down in accordance with the invention at an average rate exceeding the required minimum average rate of approximately 5° C./sec. (see FIG. 3), i.e., at a rate of approximately 100° C./sec. and the coercive force of the particles at room temperature was found to be 685 oersteds. According to the X-ray diagram such particles consist entirely of the hexagonal phase of the Fe_2P -structure. When the melt was cooled down at an average rate lower than the required minimum average rate of approximately 5° C./sec. at room temperature a coercive force of only 25 oersteds was obtained and the particles consisted, according to the X-ray diagram, of two phases, viz. the hexagonal phase, and the orthorhombic phase. This clearly proves the unfavourable influence of the orthorhombic phase on the coercive force.

Example 2

A melt was formed of 95% by weight of phosphorus-copper, 3.5% by weight of iron and 1.5% by weight of cobalt containing $(\text{Fe,Co})_2\text{P}$ -particles having a Fe/Co ratio of 70:30. This melt was cooled in accordance with the invention at an average rate higher than the required minimum average rate of approximately 130° C./sec. (see FIG. 3), i.e., at an average rate of approximately 200° C./sec. The coercive force of the particles at room temperature was found to be 275 oersteds and the particles consisted substantially completely of the hexagonal phase. When the melt was cooled down at an average rate of 40° C./sec., i.e., at an average rate below the required minimum average rate, the coercive force at room temperature was found to be only 143 oersteds and the particles consisted of the hexagonal and orthorhombic phases.

Example 3

A melt was formed of 95% by weight of phosphorus-copper, 3.75% by weight of iron and 1.25% by weight of cobalt containing $(\text{Fe,Co})_2\text{P}$ -particles having a Fe/Co ratio of 75:25. After the melt was cooled down at an average rate higher than the required minimum average rate of approximately 75° C./sec. (see FIG. 3), i.e., an average rate of approximately 200° C./sec. the coercive force at room temperature was found to be 735 oersteds and the particles consisted completely of the hexagonal phase. After cooling down at an average rate of 40° C./sec., i.e., an average rate lower than the required minimum average rate, the particles were found to consist of both the hexagonal and orthorhombic phases and the coercive force at room temperature was only about 326 oersteds.

Example 4

A melt was formed of 99% by weight of phosphorus-copper, 0.85% by weight of iron and 0.15% by weight of cobalt and was granulated in water to globules having a diameter of from about 0.3 to 0.6 mm. These granules were lixiviated with dilute HNO_3 (1:2) and subsequently the powder was heated for 2 hours at 450° C. The intrinsic coercive force H_C of the powder was 3200 oersteds. A permanent magnet was formed by compressing this powder in a magnetic field of 6000 oersteds to a density

of approximately 70%. After the compression treatment the magnet was heated again for 2 hours at 400° C. and was found to have the following magnetic properties: $B_r=3950$ gauss, $H_C=2400$ oersteds, $B_H C=1920$ oersteds and $BH_{\text{max.}}=3.1 \times 10^6$ gauss-oersteds.

While we have described our invention in connection with specific examples we do not desire to be limited thereto as obvious modifications will readily present themselves to one skilled in this art.

What is claimed is:

1. In the manufacture of permanent magnets from separate particle-size magnets containing the hexagonal phase of the compound $(\text{Fe,Co})_2\text{P}$ as the constituent essential for the permanent magnetic properties, heating said particle-size magnets with a Fe/Co ratio between about 90:10 and 60:40 to a temperature at least between 900° C. and 1150° C., and cooling said particle-size magnets to a temperature below about 600° C. from said temperature at such an average rate greater than about 2° C./sec. as to prevent the formation at the lower temperatures of the orthorhombic phase.

2. In the manufacture of permanent magnets from separate particle-size magnets containing the hexagonal phase of the compound $(\text{Fe,Co})_2\text{P}$ as the constituent essential for the permanent magnetic properties, heating said particle-size magnets with a Fe/Co ratio between about 90:10 and 60:40 to a temperature at least between about 900° C. and 1150° C. and which increases with decreasing values of said ratio, and cooling said particle-size magnets to a temperature below about 600° C. from said temperature with an average cooling rate which increases with a decrease in said ratio and which is at least 2° C./sec. when said ratio is about 90:10 and greater than 75° C./sec. when said ratio is between about 75:25 and 60:40.

3. In the manufacture of permanent magnets from separate particle-size magnets containing the hexagonal phase of the compound $(\text{Fe,Co})_2\text{P}$ as the constituent essential for the permanent magnetic properties, heating said particle-size magnets with a Fe/Co ratio between about 90:10 and 60:40 to a temperature at least between about 900° C. and 1150° C. and which increases with decreasing values of said ratio, cooling said particle-size magnets to a temperature below about 600° C. from said temperature with an average cooling rate which increases with a decrease in said ratio and which is at least 2° C./sec. when said ratio is about 90:10 and greater than 75° C./sec. when said ratio is between 75:25 and 60:40, and heating said particle-size magnets in a non-oxidizing atmosphere at a temperature between about 650° C. and 300° C. for a time which is higher as the heating temperature is selected lower.

4. The method of claim 3 in which the heat-treated particle-size magnets are pressed into an adherent magnet body and the body is heated in a non-oxidizing atmosphere at a temperature between about 650° C. and 300° C.

5. In the manufacture of permanent magnets from separate particle-size magnets containing the hexagonal phase of the compound $(\text{Fe,Co})_2\text{P}$ as the constituent essential for the permanent magnetic properties, heating said particle-size magnets with a Fe/Co ratio between about 90:10 and 60:40 to a temperature at least between about 900° C. and 1150° C. and which increases with decreasing values of said ratio, and cooling said particle-size magnets to a temperature below about 600° C. from said temperature with an average cooling rate which increases with a decrease in said ratio and is at least 2° C./sec. when said ratio is about 90:10 and greater than 75° C./sec. when said ratio is between 75:25 and 60:40, pressing said particle-size magnets into an adherent body, and heating the body in a non-oxidizing atmosphere at a temperature between about 650° C. and 300° C.

6. The method of claim 5 in which the particle-size magnets are pressed in the presence of a magnetic field.

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