May 13, 1969 SHOTARO SHIMIZU ET AL 3,444,012

PROCESS FOR TREATING PLATINUM-IRON PERMANENT MAGNET ALLOYS FOR IMPROVING THEIR MAGNETIC PERFORMANCE

Filed June 22, 1965 Sheet 1 of 2

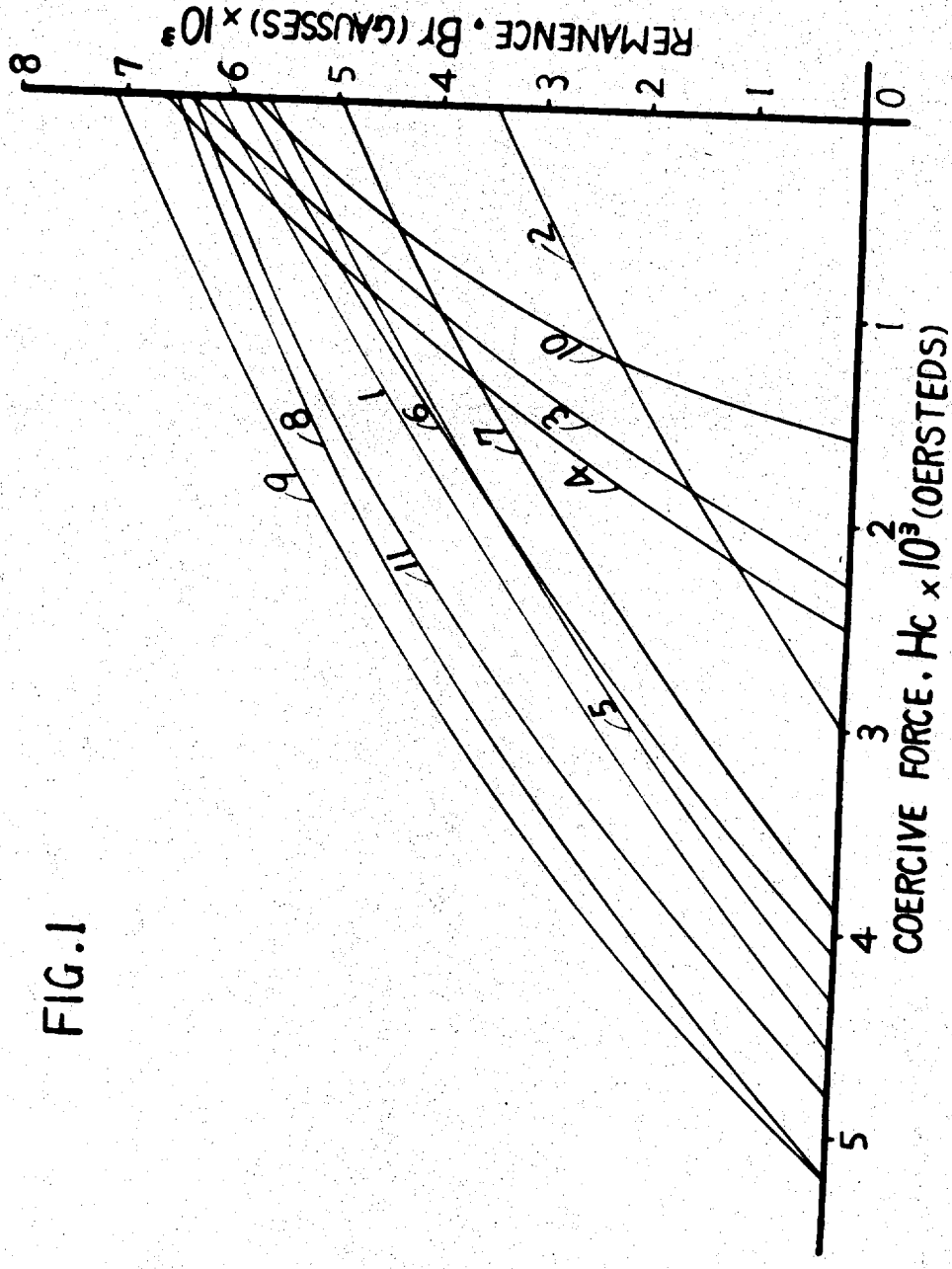
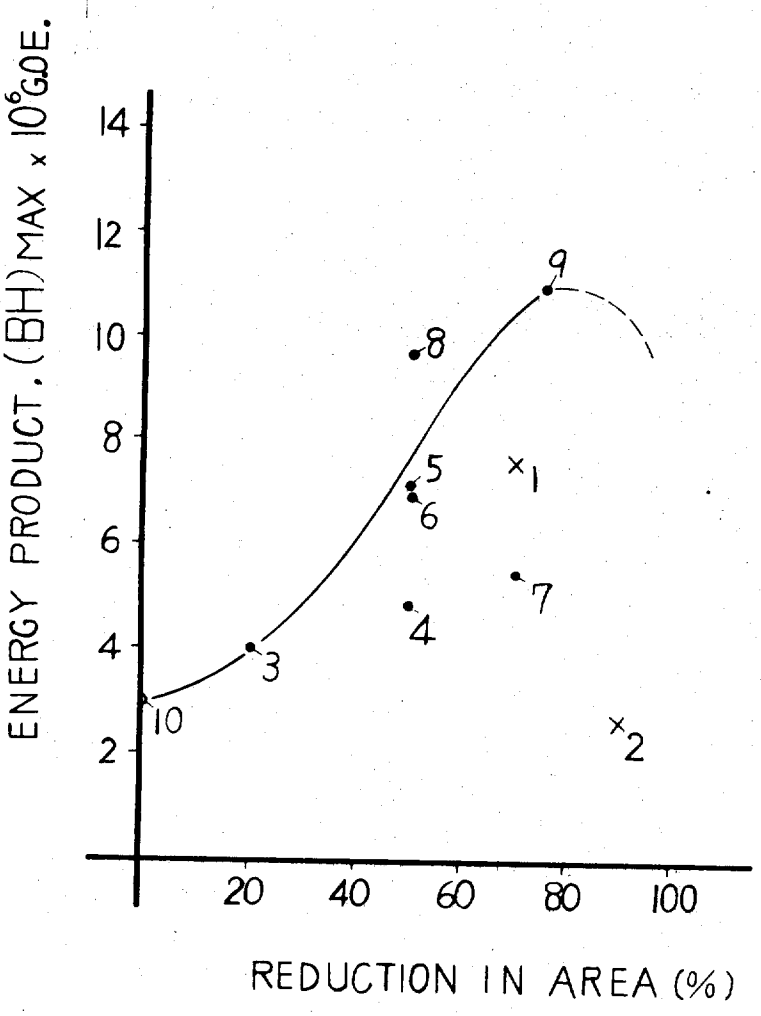


FIG. 1

INVENTORS
SHOTARO SHIMIZU & KUNIOCHI WATAI
BY
ATTORNEY

FIG. 2



INVENTORS
SHOTARO SHIMIZU & KUNIYOSHI WATAI
BY
ATTORNEY

United States Patent Office

3,444,012
Patented May 13, 1969

3,444,012

PROCESS FOR TREATING PLATINUM-IRON PERMANENT MAGNET ALLOYS FOR IMPROVING THEIR MAGNETIC PERFORMANCE

Shotaro Shimizu and Kuniyoshi Watai, Tokyo, Japan, assignors to Citizen Tokei Kabushiki Kaisha, Shinjuku, Tokyo, Japan, a corporation of Japan

Filed June 22, 1965, Ser. No. 465,894
Claims priority, application Japan, July 10, 1964, 39/39,397
Int. Cl. H01f *1/04;* C22c *5/00;* C22f *1/14*
U.S. Cl. 148—101 8 Claims

ABSTRACT OF THE DISCLOSURE

A process for treating platinum-iron alloys of the super lattice type for improving their magnetic characteristics comprising the steps of cold working a platinum-iron alloy body, to transform it from an ordered crystalline state to a substantially fully disordered state, and then subjecting said body to aging at a temperature between 400° C. and 500° C. during a predetermined period to produce in said body a final state which is partially ordered and partially disordered. Said body may include from 1–8% by weight of one or more of the elements selected from the group composed of Li, Os, Pd, Rb, Ni, Co, Au, Ag, Cu and H. Comminuting said body into a powder, forging, rolling, and swaging are disclosed as methods of cold working.

The invention relates to a process of treating platinum-iron permanent magnet alloys for improving their magnetic performance.

It is common knowledge of those skilled in the art that platinum iron as well as platinum-cobalt alloys possess superior magnetic characteristics of the super lattice type permanent magnet alloys. In practice, however, the first kind of alloys referred to above have been found as inferior in view of their reduced magnetic performance in comparison with the said second kind of magnetic alloys.

It is further commonly known that platinum-cobalt alloy of equiatomic composition has an order-disorder transition point at about 825° C., above which the alloy is in the disordered state. On the other hand, this alloy may be transferred into an ordered state by aging for a certain time duration at temperatures lower than the above-specified value. When the alloy is in an intermediate state between the above-mentioned extreme states, more specifically in a partially ordered state, it possesses a high magnetic characteristic. Thus, it will be clear that the super lattice type permanent magnetic alloys must be quenched substantially completely to the disordered state from a proper temperature higher than the transition point in order to achieve optimum magnetic characteristics by way of the aging process above referred to.

Although the platinum-iron alloy above-referred to has a high value of magnetic moment, it is inferior in comparison with platinum-cobalt alloys in that it cannot be effectively subjected to the heat disordering treatment used in connection with platinum-cobalt alloy by quenching in the disordered state at higher temperatures on account of its higher rate of transformation from on to the other state.

It was now found that the platinum-iron alloy having a disordered state can be satisfactorily produced, when the alloy is quenched from higher temperatures and then subjected to a cold plastic deformation such as, for instance, by rolling, forging, swaging, or the like, or alternatively to mechanical size-reducing treatment such as, for instance, filing, ball-milling or the like. When the

thus obtained platinum-iron alloy having a disordered state is further subjected to a proper aging treatment, as will be specifically described hereinafter by way of examples, it shows a remarkably high magnetic performance. Thus realized magnetic characteristics are superior to than those of platinum-iron alloys which have been subjected to a conventional treatment comprising both a quenching and a subsequent aging step. The magnetic performance of the platinum-iron alloy treated according to this invention is comparable to or even higher than that of conventionally used platinum-cobalt alloys.

Although the alloys subjected to the treatment according to this invention contain in general two specific elements, platinum and iron, in a substantially equiatomic ratio, they may include 1–8% in toto of one or more additives such as Co, Ni and/or H for improving the quenchability of the alloys.

To the platinum-iron alloys, one or more further specific elements such as Au, Ag and Cu may be added in quantities of 1–8% in toto, separately from or in combination with the said quenchability-improving additives, for the purpose of improving the plasticity of the alloys to be treated according to the novel technique.

Separately from or in combination with the above-mentioned additives, a small quantity, say, 1–7% in total including the above-additives, of one or more selected members from the group consisting of Ir, Os, Pd and Rh, may be added to the alloys to be treated according to the novel process of the invention.

As for the composition of the basic elements of the platinum-iron alloys, optimum results can be obtained with an equiatomic composition.

For better and clearer understanding of the present invention, several numerical examples will be given hereinbelow for the purpose of illustration, but not in a limiting sense. At the same time, the obtained specific results are shown in the accompanying drawings, in which:

FIG. 1 is a diagram showing magnetic properties of selected nine alloys treated according to the present novel technique, with two conventional alloys being included for comparison; and

FIG. 2 is a diagram showing the improved effects according to this invention as a function of the reduction in areas as caused by the cold plastic deformation.

Example 1

1 kg. of a platinum-iron alloy having an equiatomic composition, that is a ratio of 77:23 by weight was melted in an induction melting furnace and poured into a mold so as to produce ten cylindrical ingots, 10 cm. long and having a diameter of 10 mm. By means of a file, one of these cylindrical ingots was transformed into a coarse powder of a mean particle size of about 150 microns. The filing powder was then compressed in a press under a pressure of 10 tons per square centimeter so as to form a solid cylinder of the same size as above specified. This compacted cylinder was then subjected to an aging treatment at 400° C. for about an hour. This formed and treated sample possessed high and favorable magnetic characteristics as shown in first line of the Table 1 and illustrated by curve 1 in FIG. 1 of the accompanying drawings.

Example 2

100 grs. of the filing powder prepared in Example 1 was further subjected to a ball-milling operation so as to produce a still finer powder having a mean particle size of about 2–5 microns. This powder was then compacted in the same way as described in Example 1, aged at 500° C. for an hour. The resultant product showed magnetic performance as listed in the second line of the Table 1 and illustrated by curve 2 in FIG. 1.

Example 3

One of the cylindrical ingots prepared in Example 1 was subjected to a cold forging step so as to produce a solid square bar of 8 x 8 mm. cross-section. By this deforming treatment, the alloy showed magnetic properties as listed in the third line of the Table 1, and illustrated by curve **3** in FIG. 1.

Example 4

A plate, 5 mm. thick, was machined out of an ingot obtained in Example 1 and rolled to reduce the thickness to 2.5 mm. The rolled sample was then subject to an aging treatment at about 500° C. for about an hour. The processed product showed magnetic characteristics as shown in the fourth line in the Table 1 and illustrated by curve **4** in FIG. 1.

Example 5

One of the ingots prepared in Example 1 was covered with a thin non-magnetic sleeve and the assembly was swaged to reduce the diameter thereof from 11 to 7.5 mm. The thus mechanically reduced sample produced by cold working of the material showed superior magnetic properties as shown in the fifth line of the Table 1 and by curve **5** in FIG. 1.

Example 6

An alloy comprising 72 wt. percent platinum, 23 wt. percent iron and 5 wt. percent palladium, was melted in a high frequency induction furnace and poured into molds so as to form 10 mm.-cylindrical solid ingots. These ingots were water-quenched from 1300° C. and then swaged to 7 mm. diameter. These swaged and reduced products were aged at 500° C. for an hour. The final products showed superior magnetic properties as shown in the sixth line of the Table 1 and by curve **6** in FIG. 1.

Example 7

A mass of an alloy comprising platinum 73 wt. percent, iron 21 wt. percent and gold 3 wt. percent was melted similarly as before and poured into ingots of a diameter of 10 mm. These ingots were water-quenched from 1300° C., swaged to solid cylinders of a diameter of 6 mm. and aged at 500° C. for an hour. These products showed superior magnetic properties as shown in the seventh line of the table and by curve **7** in FIG. 1.

Example 8

A mass of platinum 77 wt. percent, iron 13 wt. percent and cobalt 10 wt. percent was melted similarly as before and poured into ingots of a diameter of 10 mm. Several of these ingots were water-quenched from 1300° C. and swaged to reduce their diameter to 7 mm., and then aged at 400° C. for an hour. The final products showed superior magnetic properties as shown in eighth line of the table and by curve **8** in FIG. 1.

Example 9

Several ingots prepared in Example 8 were heated to 1300° C. in hydrogen atmosphere so as to absorb hydrogen to a saturating degree, water-quenched as before, swaged to reduce their diameter to 5 mm. and aged at 400° C. for an hour. The final products showed superior magnetic properties as shown in the ninth line of the table and by curve **9** in FIG. 1.

The range of the degree of cold plastic deformation of the material according to the foregoing, being expressed in terms of reduction in cross-sectional area, is shown by Table 2 and illustrated by FIG. 2. From these data, the obtained improvements in magnetic properties will be obvious. In the evaluation of the data corresponding to foregoing Examples 1 and 2, the reduction in area was estimated from the values of residual stress as observed after the deforming treatment.

As will be noted, the larger the reduction in area, the greater the improvement of magnetic properties of the products obtained. The least improvement could be observed with 20% of the reducing value, yet higher values than 50% appreciably contribute to the desired results In Examples 1 and 2, the improvements are rather low on account of lower density values of the samples under test. In Table 2 and FIG. 2, sample No. 10 is of a conventional platinum nickel alloy.

TABLE 1

Sample No.	Br. gausses	Hc, oersteds	Hci, oersteds	$(BH)\times10^6$ $G._{max}$·Oe.	Density, g./cm.^{3}
1	6,200	4,600	7,400	7.6	13.0
2	3,500	3,000	8,800	2.7	9.2
3	6,400	2,300	3,200	4.0	14.9
4	6,700	2,500	3,500	4.9	14.8
5	5,700	4,300	7,700	7.2	14.0
6	5,900	4,100	7,300	7.0	14.6
7	5,000	3,900	6,800	5.5	14.5
8	6,500	5,200	7,200	9.7	14.8
9	7,100	5,200	7,300	11.0	14.8
10*	5,830	1,570	1,800	3.1	15.0
11*	6,400	4,800	6,500	9.2	15.5

*Samples 10 and 11 are conventional platinum-cobalt as described in "Material in Design Engineering", July 1959, page 110.

TABLE 2

Sample No.	Reduction in area, percent	(BH) max
1	*70	7.6×10^6 G.Oe.
2	*90	2.7
3	20	4.0
4	50	4.9
5	50	7.2
6	50	7.0
7	65	5.5
8	50	9.7
9	75	11.0
10	0	3.1

*Estimated values inversely from obtained magnetic properties.

It is to be understood that the treating steps disclosed in the several foregoing examples are illustrative of the application of the principles of the invention.

What is claimed is:

1. A process for treating platinum-iron alloys of the super lattice type for improving their magnetic characteristics comprising the steps of cold working a platinum-iron alloy body to transform it from an ordered crystalline state to a substantially fully disordered state, and then subjecting said body to aging at a temperature between 400° C. and 500° C. during a predetermined period to produce in said body a final state which is partially ordered and partially disordered.

2. A process as claimed in claim **1**, said body having an equiatomic composition and said aging period being about one hour.

3. A process as claimed in claim **1**, said body including from 1–8% as to weight of one or more of the elements selected from the group composed of Li, Os, Pd, Rh, Ni, Co, Au, Ag, Cu and H.

4. A process as claimed in claim **1**, said body being produced by melting and castnig of the initial alloys of equiatomic composition, and said cold working step consisting of comminuting said body into a powder having a mean particle size of the order of 100–200 microns and compacting said powder into a solid body prior to subjecting the same to said aging step.

5. A process as claimed in claim **1**, said body being produced by melting and casting of the initial alloy of equiatomic composition, and said cold working step comprising initially comminuting said body by file treatment into a powder having a mean partical size of 100–200 microns, further comminuting said powder by ball milling to a final particle size of 2–5 microns, and compacting the final powder into a solid body prior to subjecting the same to said aging step.

6. A process as claimed in claim **1**, said body being produced by melting and casting of the initial alloy of equiatomic composition, and said cold working step consisting of substantially reducing the size of said body by cold forging prior to subjecting the same to said aging step.

7. A process as claimed in claim 1, said body being produced by melting and casting of the initial alloy of equiatomic composition, and said cold working step consisting of cold rolling said body into sheet form prior to subjecting the same to said aging step.

8. A process as claimed in claim 1, said body being produced by melting and casting into a rod of the initial alloy of equiatomic material, and said cold working step consisting of inserting said rod in a sleeve of non-magnetic material and reducing the diameter thereof by swaging prior to subjecting the same to said aging step.

References Cited

UNITED STATES PATENTS

1,669,649	5/1928	Beath	148—126 XR
2,192,744	3/1940	Howe	148—101 XR
2,289,570	7/1942	Boegehold	148—105 XR
2,617,723	11/1952	Studders	148—101 XR
2,622,050	12/1952	Martin	148—102
3,206,337	9/1965	Walmer	148—101 XR

OTHER REFERENCES

Gratsianov et al., The Physics of Metals and Metallography, vol. 17, n4, April 1964, pp. 38–44. (Translation of Fiz. Metal. Metalloved published April 1964.)

The Platinum Metals and Their Alloys, R. F. Vines, 1941, published by Int. Nickel Co., pp. 58–62 and 74–78.

Fundamental Principles of Powder Metallurgy, W. D. Jones, 1960, published by Arnold Ltd., pp. 176–180.

L. DEWAYNE RUTLEDGE, *Primary Examiner.*

PAUL WEINSTEIN, *Assistant Examiner.*

U.S. Cl. X.R.

75—172, 200; 148—31.57, 102, 103, 105, 120, 121, 126