Aug. 31, 1965 HAKARU MASUMOTO ETAL 3,203,838

METHOD OF MANUFACTURING PERMANENT MAGNETS HAVING LARGE COERCIVE FORCE

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Fig. 1.

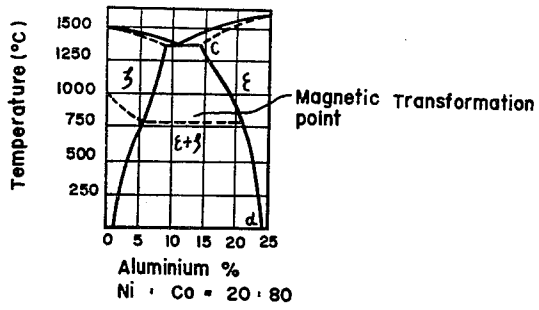

Fig. 2.

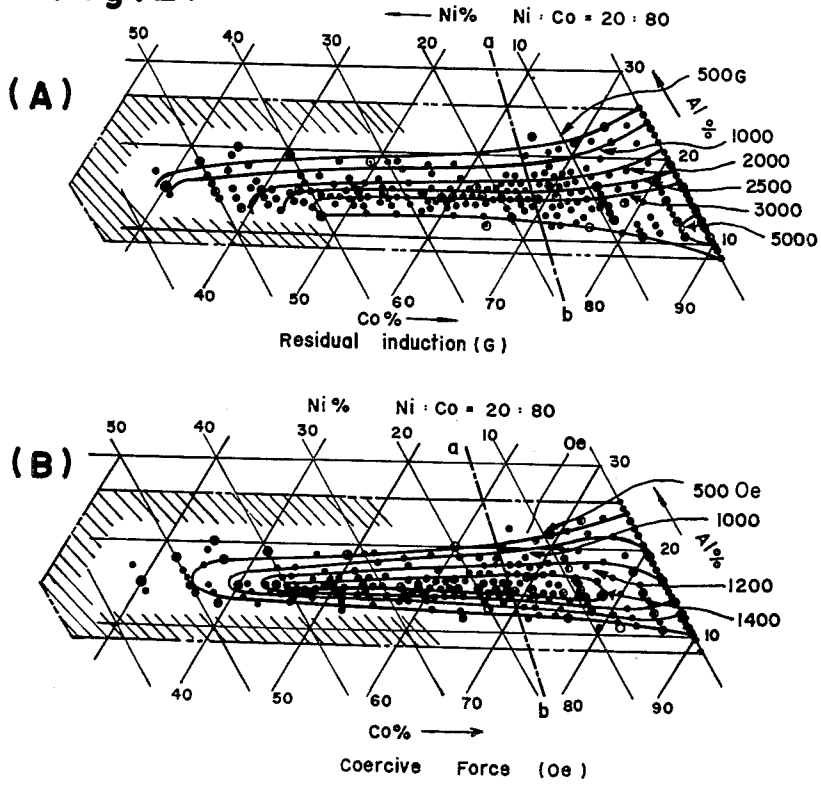

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Fig. 3.

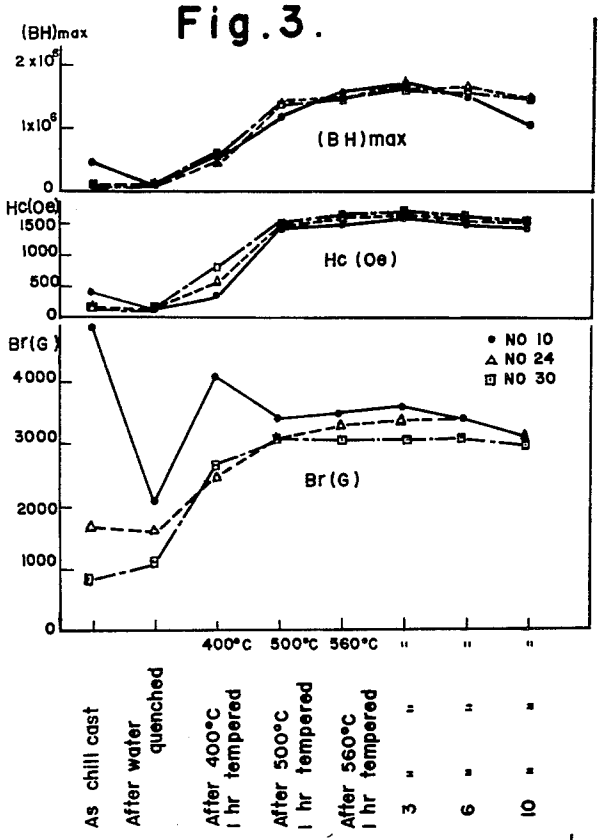
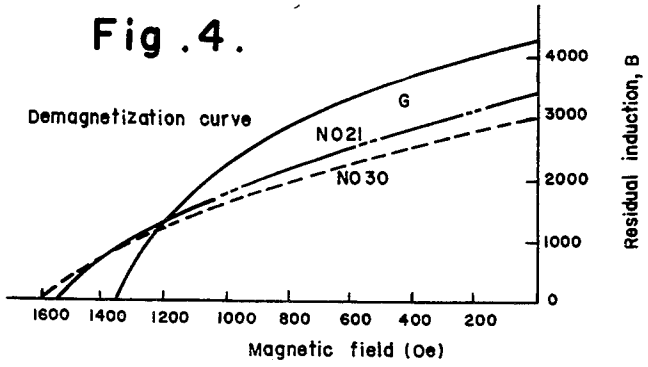


Fig. 4.



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3,203,838

METHOD OF MANUFACTURING PERMANENT MAGNETS HAVING LARGE COERCIVE FORCE

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5 Claims. (Cl. 148—101)

The present invention relates to a method of manufacturing permanent magnets having a large coercive force, more particularly, to permanent magnets consist ing essentially of about 20 to 92% of Co, 7.9 to 26% of Al and nickel in an effective amount up to about 65%.

The principal object of the invention is to obtain permanent magnets having large coercive force more easily and at a lower cost.

Heretofore known single domain particle magnets are compressed iron powder magnets, compressed Fe-Co powder magents, Bismanol (Mn-Bi alloys) and Ferroxdure ($BaO.6Fe_2O_3$), all of which have pretty large residual induction (Br) and coercive force (Hc), but in manufacturing such magnets it is necessary to prepare at first very fine, but suitable sized magnetic particles, then the powder should be compressed with an appropriate pressure and some of them should be sintered further at a higher temperature. More particularly, in the former two magnets it is very difficult to produce fine particles of a desired size and the method of its manufacture is pretty complicated, in other words, the above known magnets have disadvantages that the manufacture is generally very complicated and difficult and moreover, can not give always the product having the same characteristics.

In order to overcome the above described difficulties, the inventors have selected such alloys which precipitate single magnetic domain particle phase in the matrix of non-magnetic property by a simple heat treatment and tried to obtain single domain particle magnets having a large coercive force and found that Co-Al alloys containing 10 to 25% Al is adapted to the object of the invention and shows a very large coercive force such as 1,320 oersteds by subjecting to a proper treatment.

The inventors made further investigations by adding Ni to the Co-Al alloys and accomplished to find out single domain particle magnets having much larger coercive force.

In carrying out the invention into effect, a colbalt-aluminum-nickel ternary alloy consisting essentially of about 20 to 92% of cobalt, about 7.9 to 26% of aluminum and an effective amount up to about 65% of nickel, after casting in a metal or sand mold or the like to be quickly cooled or after heat treating at a temperature above the solid solubility line for a suitable time to produce a homogeneous solid solution structure and quenching in air, water or oil or other suitable fluid medium, is heated to a temperature above 350° C. for a suitable time, or when the alloy is cast in a mold, or when the alloy is plunged into a suitable medium after being subjected to said solid solution treatment, the cooling speed is properly reduced to precipitate ferromagnetic fine particles in the non-magnetic matrix, thereby providing permanent magnets having large coercive force.

The accompanying drawings illustrate curve diagrams showing the properties of the alloys of the invention, of which–

FIG. 1 illustrates the sectional diagram of Ni:Co=20:80 in the Co-Al-Ni ternary equilibrium diagram (*a–b* section in FIG. 2);

FIGS. 2(A) and (B) show equi-value curves statistically found from the measured magnetic values (black points illustrate the composition of the measured alloy);

FIG. 3 shows curves illustrating the relation between the magnetic property and the tempering temperature and time for alloys No. 10, No. 24 and No. 30 in the table, and

FIG. 4 shows the demagnetization curves of the alloys G, No. 21 and No. 30 in the table.

Now the results of investigations made by the inventors will be explained in detail.

At first, in order to manufacture the alloy of the invention a suitable amount of Co and Ni was melted in air, inert gas or vacuum by using a suitable melting furnace, then a small amount of degassing agent such as Mn, Si, Al or Ti was added to eliminate gasses, then further a suitable amount of Al was added and thoroughly agitated, thereby obtained molten alloy having homogeneous structure, then the melt was poured into a mold of a suitable shape and size to provide a sound ingot or product. According to the composition the forgeable ingot was forged at a suitable high temperature to provide the product of a desired shape.

Next, the above casting or forging was heated at a suitable temperature higher than the solid solubility line *c–d* in FIG. 1, thereby its greater part becomes ϵ solid solution. Then they were heated at a suitable temperature lower than the *c–d* solid solubility line and within the region of $\epsilon+\zeta$ to precipitate single magnetic domain particles of ζ phase in a non-magnetic matrix of ϵ. The product thus obtained, when it is magnetized in a strong magnetic field, showed a large coercive force such as 1,600 oersteds (Oe) at the maximum and provided the magnet having a greater coercive force than that of Co-Al binary alloy.

Referring to FIGS. 2(A) and (B) there are shown compositions of a number of alloys melted in air by black points and the curves are of equimagnetic value statistically obtained from the results measured about the magnetic properties of these alloys. The properties of the typical alloys (points of larger circles in FIG. 2) are shown in the following table:

Further, the following relation is obtained from FIGS. 2(A) and (B).

Co(percent)	Al (percent)	Ni(percent)	Br(G)	Hc(Oe)
20 –92	7.9–26	0–65	1,000–4,300	200–1,600
36 –89	11 –24	0–49	1,200–6,000	500–1,600
37 –88	12 –22	0–48	1,500–5,800	800–1,600
39 –87	12.5–20.5	0–46	1,800–5,300	1,000–1,600
42 –86	13 –18	0–43	2,200–4,500	1,200–1,600
44.5–78	14 –17	7–40.5	2,500–3,400	1,400–1,600

Accordingly, Co-Al-Ni alloys of the invention may be classified into such alloys consisting of 20 to 92% Co, 7.9 to 26% Al, an effective amount up to 65% Ni; alloys consisting of 36 to 89% Co, 11 to 24% Al, an effective amount up to 49% Ni; alloys consisting of 37 to 88% Co, 12 to 22% Al, an effective amount up to 48% Ni; alloys consisting of 39 to 87% Co, 12.5 to 20.5% Al, an effective amount up to 46% Ni; alloys consisting of 42 to 86% Co, 13 to 18% Al, an effective amount up to 43% Ni; alloys consisting of 44.5 to 78% Co, 14 to 17% Al, 7 to 40.5% Ni, these alloys can develop the required magnetic properties by the heat treatment of the invention.

Mark of alloys	Composition (percent)			Tempering treatment		Br (G)	Hc (Oe)	(BH) max. (×10⁶) BrOe	Remarks
	Co	Al	Ni	° C.	Hr.				
C	88.3	11.7	0	500	2	5,100	650	1.19	Forgeable.
D	87.8	12.2	0	500	4	5,700	800	2.02	Do.
F	86.4	13.6	0	550	4	4,800	1,050	2.11	Somewhat forgeable.
G	85.4	14.6	0	550	4	4,300	1,320	2.38	
H	83.4	16.6	0	550	3	3,800	1,310	2.02	Unforgeable.
I	80.4	19.6	0	500	16	2,400	1,200	1.00	Do.
1	86.7	10.8	2.5	560	1	4,500	380		Forgeable.
2	84.8	12.6	2.6	560	3	5,000	1,200	1.88	Do.
3	82.9	14.5	2.6	560	3	4,000	1,400	2.20	Unforgeable.
4	79.7	17.8	2.5	560	3	3,000	1,350	1.15	Do.
5	71.5	23.1	5.4	570	3	1,000	300		Do.
6	82.2	10.8	7.0	560	1	3,500	350		
7	78.5	14.3	7.2	560	3	3,600	1,420	1.84	Unforgeable.
8	79.7	11.0	9.3	560	3	2,700	300		
9	78.6	12.4	9.0	560	3	3,800	1,300	1.55	Forgeable.
10	76.4	14.5	9.1	560	3	3,500	1,500	1.65	Somewhat forgeable.
11	75.0	15.8	9.2	560	3	3,200	1,580	1.55	Unforgeable.
12	69.7	21.2	9.1	570	3	900	500		Do.
13	74.2	14.5	11.3	560	3	3,400	1,500	1.64	Somewhat forgeable.
14	76.2	11.8	12.0	560	1	3,400	580		Forgeable.
15	64.7	22.1	13.2	570	3	600	500		Unforgeable.
16	71.1	14.7	14.2	560	3	3,400	1,500	1.63	Forgeable.
17	69.5	16.4	14.1	560	6	3,000	1,500	1.50	Unforgeable.
18	69.0	14.7	16.3	560	3	2,800	1,580	1.45	Forgeable.
19	67.2	14.6	18.2	560	3	3,600	1,450	1.64	Do.
20	67.2	12.8	20.0	560	3	3,800	870		Do.
21	65.1	14.7	20.2	560	3	3,400	1,550	1.73	Unforgeable.
22	60.0	20.0	20.0	570	3	700	500		Forgeable.
23	62.1	15.8	22.1	560	3	2,500	1,600	1.42	Do.
24	65.3	14.5	22.2	560	3	3,300	1,550	1.62	Do.
25	65.0	11.8	23.2	560	1	3,000	300		
26	59.0	14.7	26.3	560	3	3,000	1,560	1.52	Forgeable.
27	57.1	14.7	28.2	560	3	3,000	1,550	1.52	Do.
28	53.1	14.6	32.3	560	3	3,100	1,580	1.53	Do.
29	49.5	18.3	32.2	560	6	500	300		Unforgeable.
30	50.4	14.5	35.1	560	6	3,000	1,600	1.55	Forgeable.
31	47.2	12.8	40.0	560	1	3,000	400		Do.
32	41.2	18.7	40.1	560	6	500	400		Unforgeable.
33	44.2	14.8	41.0	560	6	2,700	1,580	1.30	Forgeable.
34	40.2	14.7	45.1	560	3	2,200	1,300	0.80	Do.
35	37.5	17.4	45.1	560	6	700	500		Unforgeable.
36	35.0	20.0	45.0	570	6	0	0		Do.
37	39.2	12.7	48.1	560	3	1,400	200		Forgeable.
38	35.3	14.7	50.0	560	3	1,200	750		
39	32.2	17.5	50.3	560	6	500	200		
40	29.8	15.2	55.0	560	3	700	200		

Next, FIG. 3 illustrates characteristic curves showing the results of experiments about the change of magnetic properties according to the change of tempering temperature and time after the solid solution treatment of the alloys No. 10, No. 24 and No. 30 having a large coercive force.

As apparent from the table and the curves, the values of Br and (BH)max. decrease by the addition of Ni to the Co-Al binary alloys but the coercive force increases to a substantial value, that is, it will be apparent that according to the invention, a considerably large coercive force can be obtained by a simple method of manufacturing the alloy and heat treatment. In case of metal mold casting and water quenching in FIG. 3 the cooling speed is considerably large so that fine particles in ζ phase do not substantially precipitate and magnetic property is considerably inferior but if the cooling speed is properly reduced somewhat excellent properties can be obtained without further subjecting to the tempering.

FIG. 4 illustrates the demagnetization curves of the alloys G, No. 21 and No. 30. As seen from the table, when the content of Al is comparatively small, the alloy is forgeable, but as the content of Al increases, the forging becomes difficult and as Al increases further the forging becomes substantially impossible, and those alloys have pretty low specific gravity as they contain Al.

The reason why the Al content is limited to 7.9 to 26% in the invention is due to the fact that when Al is less than 7.9% and increases more than 26% the alloy decreases the coercive force and the residual induction as apparent from FIGS. 2(A) and (B), so that Al was limited as defined.

Co was limited to 20 to 92% by the reason that at more than 92% and less than 20% the coercive force and residual flux are reduced.

The reason why the Ni content was limited to 65% is based on the fact that at more than 65% Ni the residual induction and coercive force are reduced as shown in FIGS. 2(A) and (B).

In short, in the method of the invention, the alloy consisting essentially of about 20 to 92% Co, 7.9 to 26% Al and an effective amount up to 65% Ni and a small amount of impurities, after it is cast in a metal or sand mold or the like to be rapid-cooled, or after quenched from a high temperature above the solid solubility line by a suitable method to be made as solid solution, is tempered at a suitable temperature below the solid solubility line within the $\epsilon+\zeta$ binary region for a suitable period or when cast in a metal mold or sand mold, or when cooled to a room temperature from the temperature above the solid solution line, the cooling speed is suitably reduced to precipitate single domain particles of ferromagnetic properties in the non-magnetic matrix of ϵ, thereby attaining to develop very high coercive force, such as 1,600 oersteds and the residual induction is substantially larger than that of the ferrite magnets, thus the invention has specialities and large advantages industrially since the method of the invention is most suitable for the production of specially short magnets and enabling forging by

the selection of composition and reducing the specific gravity.

What we claim is:

1. A method of manufacturing high coercive force permanent magnets, comprising heating an alloy consisting essentially of about 20–92% cobalt, 7.9–26% aluminum, and an effective amount up to about 65% nickel to a temperature above the $\epsilon+\zeta$ binary region, quenching the alloy to a temperature below the upper boundary of the $\epsilon+\zeta$ binary region, heating the alloy in said binary region at a temperature sufficient to precipitate fine particles of ferromagnetic ζ in a matrix of nonmagnetic ϵ, and magnetizing the product thus obtained in a strong magnetic field to obtain a permanent magnet having high coercive force.

2. A method as claimed in claim 1, in which said alloy consists essentially of about 36–89% cobalt, 11–24% aluminum, and an effective amount up to about 49% nickel.

3. A method as claimed in claim 1, in which said alloy consists essentially of about 42–86% cobalt, 13–18% aluminum, and an effective amount up to about 43% nickel.

4. A method as claimed in claim 1, in which said alloy consists essentially of about 44.5–78% cobalt, 14–17% aluminum, and 7–40.5% nickel.

5. A method as claimed in claim 1, in which said temperature is above about 350° C.

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