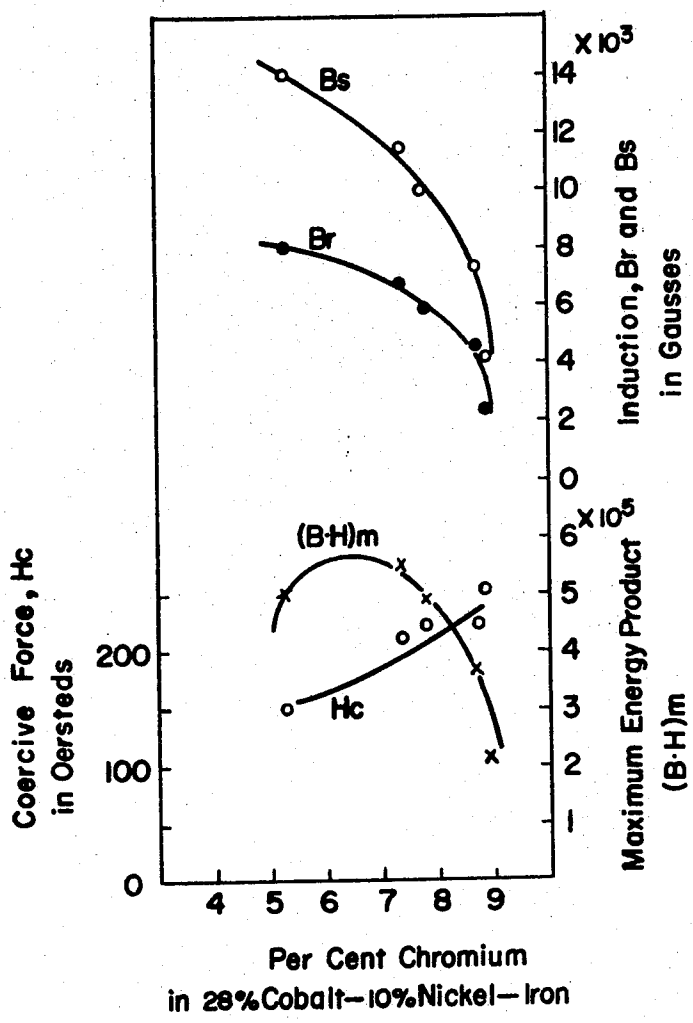
June 27, 1972 JIRO MATSUMOTO ET AL 3,673,010

COLD-WORKABLE PERMANENT MAGNET ALLOY

Original Filed May 15, 1967 4 Sheets-Sheet 1

Fig. 1



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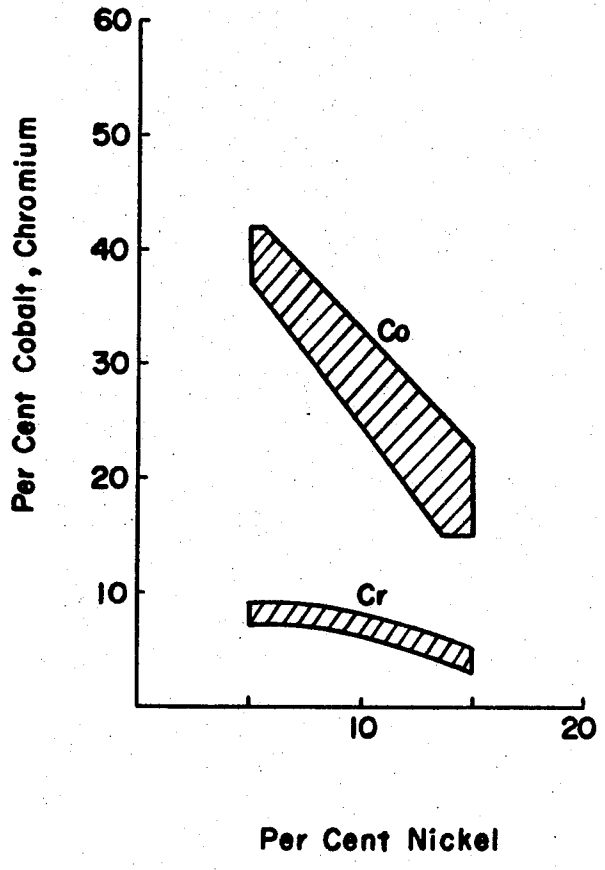
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COLD-WORKABLE PERMANENT MAGNET ALLOY

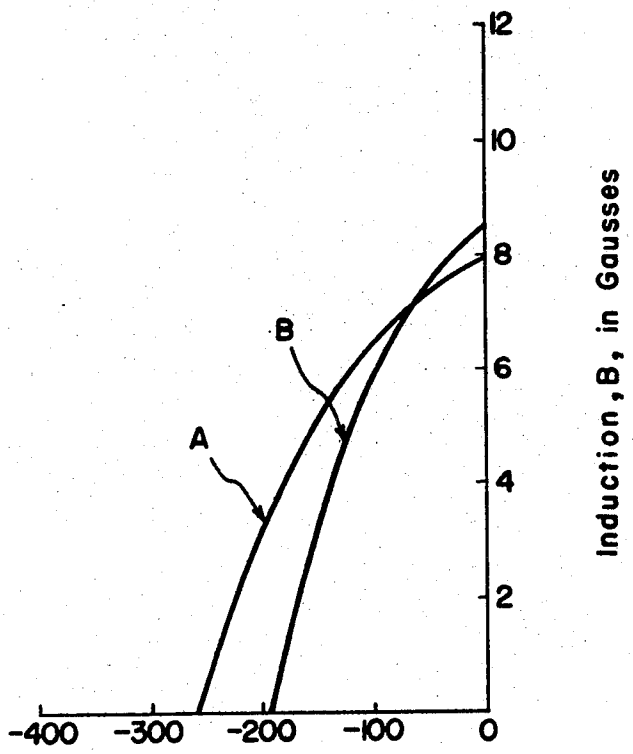
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Fig. 2



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Fig. 3

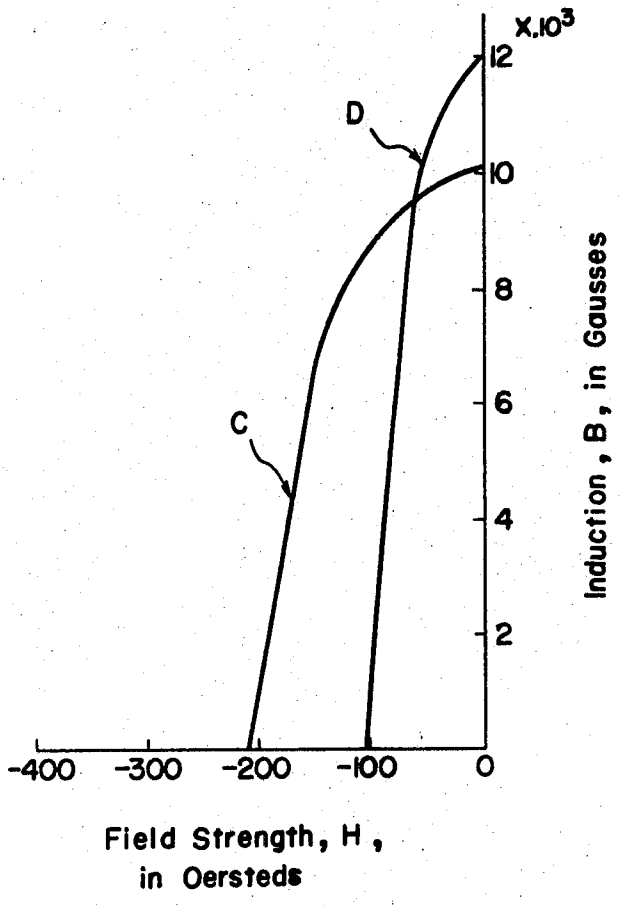


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COLD-WORKABLE PERMANENT MAGNET ALLOY

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Fig. 4



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COLD-WORKABLE PERMANENT MAGNET ALLOY

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Continuation of application Ser. No. 638,199, May 15, 1967. This application May 19, 1970, Ser. No. 34,513

Int. Cl. C22c *39/12*; H01f *1/04*

U.S. Cl. 148—31.57 1 Claim

ABSTRACT OF THE DISCLOSURE

A permanent magnet alloy mainly containing Co, Ni, Cr and Fe and having a replacement relation between Co and Ni of Co wt. percent=50–2.5(Ni wt. percent)~53–1.5(Ni wt. percent), which can very easily be subjected to mechanical working and cold working and yet is very cheap owing to the presence of less than 1% by weight of V contrary to Vicalloy containing 10–14% by weight of V.

This application is a continuation of application Ser. No. 638,199, filed May 15, 1967, now abandoned.

The present invention relates to a permanent magnet alloy which can be subjected to mechanical working and cold working in an extremely easy manner and is less expensive.

Vicalloy has been worked into a wire, a thin plate etc. and used as permanent magnet materials for measuring instruments. The use of the Vicalloy has recently been remarkably extended into the field of a semistationary memory, a hysteresis motor etc. in accordance with development of the automatic control technics.

Vicalloy is a permanent magnet material transformed into α phase by quenching and cold working and hence subjected to aging at the $\alpha+\gamma$ two-phase field to precipitate γ phase in the matrix of α phase and thus become magnetically hardened.

However, Vicalloy contains 50–52% by weight of Co and 10–14% by weight of V so that it has disadvantage of considerable expense.

The principal object of the invention is to obviate the above disadvantages of Vicalloy and provide a permanent magnet alloy which can very easily be subjected to mechanical working and cold working and yet is very cheap.

The inventors paid attention to the $\alpha+\gamma$ two-phase field of Fe-Co-Ni system alloy and after elaborate experiments have found out that if a suitable amount of Cr, Mo, V etc. are added to the Fe-Co-Ni system alloy, a series of permanent magnet materials each having an excellent workability and magnetic characteristics comparable with those of Vicalloy can be obtained in a less expensive manner.

For a better understanding of the invention reference is taken to the accompanying drawings, in which:

FIG. 1 shows curves illustrating relations between Cr content of the permanent magnet according to the invention and magnetic characteristics thereof;

FIG. 2 is a diagram showing ranges covered by compositions Co, Ni and Cr of the permanent magnet according to the invention; and

FIGS. 3 and 4 are demagnetization curves of the permanent magnets according to the invention.

The invention will now be explained with reference to examples of permanent magnet alloy embodying the invention.

Compositions, magnetic characteristics and aging temperatures of some samples of Fe-Co-Ni-Cr system alloy according to the invention are listed in the following Table 1.

TABLE 1

	C (percent)	Co (percent)	Ni (percent)	Cr (percent)	Coercive force Hc (oe.)	Residual induction Br (G)	Aging temperature (° C.)
Sample Number:							
1	0.048	40.00	5.50	7.74	185	5,900	600
2	0.038	41.08	5.39	6.50	160	8,900	600
3	0.026	31.90	10.23	7.71	200	6,600	600
4	0.022	30.36	10.34	6.89	135	9,150	600
5	0.026	22.48	14.52	6.40	175	7,450	550
6	0.023	24.70	14.90	4.00	80	9,650	550
7	0.021	10.35	19.85	3.94	55	7,300	550
8	0.016	10.76	19.20	2.19	25	7,550	550

In order to obtain the samples having the magnetic characteristics shown in the above Table 1, 5 kg. of an ingot melted in air was subjected to hot forging and rolling treatments and then quenched from a temperature of 850–1050° C. and subsequently aged at a temperature of 500–650° C. As can be seen from the Table 1, it is important that the magnet alloy according to the invention has a given composition ratio between Co, Ni and Cr.

The inventors have experimentally ascertained that the composition ratio between Co and Ni of the magnet alloy according to the invention can be given by the following formula.

$$\text{Co wt. percent} = 50 - 2.5(\text{Ni wt. percent}) \sim 53 - 1.5(\text{Ni wt. percent})$$

The amount of Cr to be added is also limited to certain range dependent upon the amount of Co and Ni. For example, the magnetic characteristics of 28% Co–10% Ni-Fe magnet alloy become maximum if about 6.5% by weight of Cr is added as shown in FIG. 1. If the amount of Cr is further increased, the saturation induction Bs

of the alloy becomes rapidly decreased until the alloy reaches to nonmagnetic state as shown in FIG. 1.

In case of increasing the amount of Ni to be added, it is necessary to decrease the amount of Co in dependence with the above formula showing the relation between Co and Ni and hence decrease the amount of Cr as shown in FIG. 2.

The magnet alloy according to the invention comprising 15–42% by weight of Co, 5–16% by weight of Ni and 3–9% by weight of Cr as shown by shaded areas in FIG. 2 showed particularly excellent magnetic characteristics.

Moreover, the inventors have experimentally ascertained that the magnet alloy according to the invention added with a small amount of Mo, V etc. can improve the magnetic characteristics thereof, and that a part or all of Cr may be replaced by Mo, V etc.

Compositions, magnetic characteristics and aging temperatures of other samples of Fe-Co-Ni-Cr system alloy according to the invention wherein a part or all of Cr is replaced by Mo are listed in the following Table 2.

TABLE 2

Sample No.	C (percent)	Co (percent)	Ni (percent)	Cr (percent)	Mo (percent)	Coercive force Hc (oe.)	Residual induction Br (G)	Aging temperature (° C.)
9	0.022	32.80	8.70	6.22	1.06	260	8,150	600
10	0.019	33.16	8.90	5.27	2.08	200	8,050	600
11	0.023	32.60	8.15	5.51	0.81	170	7,664	600
12	0.031	33.10	8.15	4.37	2.02	130	8,548	600
13	0.029	33.00	8.20	3.47	2.95	90	8,106	600
14	0.021	33.30	8.30	2.57	4.18	60	9,027	600
15	0.024	33.00	8.52	----	5.02	45	8,585	600
16	0.023	31.70	3.87	7.28	1.06	60	8,190	600
17	0.022	32.00	3.92	9.50	1.04	30	7,570	600
18	0.021	34.51	8.85	6.12	1.06	250	8,050	600
19	0.021	33.32	8.94	7.45	1.04	280	4,830	600
20	0.026	23.20	13.89	5.47	1.05	195	8,500	550
21	0.025	22.80	13.90	4.37	1.03	140	9,700	550
22	0.024	23.30	13.78	3.24	1.03	75	10,000	550
23	0.026	20.92	15.79	5.40	0.97	195	5,000	550
24	0.023	20.99	15.64	4.14	0.99	125	9,700	550
25	0.024	20.87	15.73	3.15	1.02	75	9,900	550

The samples shown in the Table 2 were obtained after quenched from 950° C. and subsequently aged at a temperature of 550–660° C.

Addition up to 1% by weight Mo to the Fe-Co-Ni-Cr system alloy according to the invention is very effective. But, it is not desirable to add more than 2% by weight of Mo because such amount of Mo causes to decrease the residual induction (Br) of the alloy.

Replacement of Cr by Mo causes to increase the residual induction (Br) of the alloy, but causes to decrease the coercive force (He) of the alloy. Thus, it is desirable to replace less than 4% by weight of Cr by Mo.

The samples having excellent magnetic characteristics shown in the Table 2 also satisfy the above mentioned formula showing the mutual relation between the amount of Co and the amount of Ni of the alloy according to the invention.

Compositions, magnetic characteristics and aging temperatures of further samples of Fe-Co-Ni-Cr system alloy according to the invention wherein a part or all of Cr is replaced by Mo and/or V are listed in the following Table 3.

TABLE 3

Sample No.	Co (percent)	Ni (percent)	Cr (percent)	Mo (percent)	V (percent)	Coercive force Hc (oe.)	Residual induction Br (G)	Aging temperature (° C.)
26	32.90	8.80	6.40	1.40	----	260	7,900	600
27	33.16	8.80	4.93	1.05	0.77	240	7,390	600
28	31.74	8.64	3.06	1.06	3.73	210	7,680	600
29	31.70	8.68	1.02	1.07	5.53	130	8,330	600
30	31.40	8.49	----	1.09	7.36	130	8,620	600
31	24.90	13.15	6.74	1.06	0.24	280	1,000	550
32	25.10	13.45	4.93	1.09	0.93	210	7,100	550
33	24.80	12.93	3.13	1.02	3.24	210	8,290	550
34	24.32	13.03	1.14	1.07	5.13	110	8,650	550
35	24.30	13.03	----	1.08	7.29	100	8,290	550

The samples shown in the Table 3 were obtained after quenched from 950° C. and subsequently aged at a temperature of 550–660° C.

Replacement of Cr by Mo and/or V causes to increase the residual induction (Br) of the alloy, but causes to decrease the coercive force (Hc) of the alloy in the same manner as in the case of replacement of Cr by Mo only. Even if all of Cr is replaced by Mo and V, the alloy still reserves more than 100 oe. of the coercive force (Hc). Thus, it is possible to replace all of Cr by Mo and/or V.

Both Mo and V are very expensive if compared with Cr so that it is desirable to make the amount of Mo and V to be added as small as possible.

In the permanent magnet alloy according to the invention, C is a considerably distrubing element capable of deteriorating the workability, decreasing the coercive force (Hc) and also conspicously decreasing the residual induction (Br). Thus, it is desirable to use less than 0.05% tion, C is a considerably disturbing element capable of by weight of C, but 0.1% by weight of C is permissible.

The inventors have also found out that addition of Ti, Zr, Nb to the alloy according to the invention is effective in a certain degree to obviate the above bad influences of C. These elements, however, serve to somewhat increase the coercive force (Hc) of the alloy according to the invention, but decrease the residual induction (Br).

Compositions and magnetic characteristics of still other samples of Fe-Co-Ni-Cr system alloy according to the invention wherein Ti is added are listed in the following Table 4.

TABLE 4

Sample No.	C (percent)	Co (percent)	Ni (percent)	Cr (percent)	Mo (percent)	Ti (percent)	Coercive force Hc (oe.)	Residual induction Br (G)
36	0.040	33.90	8.54	6.69	1.06	----	230	7,030
37	0.052	32.20	8.54	6.97	1.09	0.26	240	6,630
38	0.060	31.90	8.54	7.08	1.03	0.32	240	6,380
39	0.050	32.60	8.54	7.05	1.07	0.55	250	5,980

The samples shown in the Table 4 were obtaineo after quenched from 1050° C. and subsequently aged at a temperature of 600° C.

Addition of large amount of Ti causes to deteriorate the workability of the alloy according to the invention so that it is desirable to add less than 1% by weight of Ti.

Si, Al, Mn etc. are added as a deoxidizer to the alloy according to the invention, but these elements added serve to decrease the residual induction (Br) and also deteriorate the workability thereof. Thus, it is necessary to add less than 1% by weight of these elements, but less than 0.6% by weight of both Si and Mn and less than 0.2% by weight of Al are the most desirable range to be added to the alloy according to the invention.

In accordance with the invention elements such as B, Zr, Nb, Ca, Mg etc. may be added to the alloy for the purpose of improving the workability of the alloy. The inventors have found out that less than 1% by weight of one of these elements is effective to improve the workability of the alloy according to the invention without deteriorating the magnetic characteristics thereof. As well-known in the art, addition of small amount of S, Se, Pb to the alloy according to the invention makes it possible to improve the mechanical workability of the alloy.

The magnet alloy according to the invention is capable of further improving the magnetic characteristics thereof if it is subjected to cold working. That is, the magnet alloy according to the invention subjected to hot working may be quenched from γ phase field. Then, the alloy is subjected to pickling treatment to remove scales from the alloy and subjected to drawing and rolling treatments at room temperature. Subsequently, the alloy is aged at a temperature of 500–650° C. for suitable hours thus improving the magnetic characteristics. The cold working causes to somewhat decrease the coercive force (Hc) of the alloy, but remarkably increase the residual induction (Br) thus considerably improving the maximum energy product.

The samples 26–30 shown in the Table 3 are subjected to hot rolling treatment and then subjected to pickling treatment and subsequently subjected to 70% of cold rolling. The samples thus treated are aged at a temperature of 600° C. for 1 hour. The magnetic characteristics of the samples thus cold worked are shown in the following Table 5.

TABLE 5

Sample No.	C (percent)	Co (percent)	Ni (percent)	Cr (percent)	Mo (percent)	V (percent)	Coercive force Hc (oe.)	Residual induction Br (G)
26	0.027	32.90	8.80	6.40	1.04	----------	210	10,270
27	0.028	33.16	8.80	4.93	1.05	0.77	210	10,270
29	0.023	31.70	8.68	1.02	1.07	5.53	110	12,110
30	0.027	31.40	8.49	----------	1.08	7.36	110	11,850

The values of the residual induction (Br) shown in the Table 5 become remarkable increased if compared with those shown in the Table 3. In case of carrying out the cold working, however, it is necessary to use more than 50% reduction in thickness.

Examples of demagnetization curve of the magnet alloy according to the invention are shown in FIG. 3. The curve A shows the demagnetization curve of the sample No. 26 which was quenched from 950° C. and aged at a temperature of 600° C. for 1 hour. The curve B shows the demagnetization curve of the sample No. 20 which was quenched from 950° C. and aged at a temperature of 550° C. for 1 hour.

FIG. 4 shows demagnetization curves of the magnet alloys according to the invention which were subjected to 70% cold rolling and subsequently aged at a temperature of 600° C. for 1 hour. The curve C shows the demagnetization curve o fthe sample No. 26 and the curve D shows the demagnetization curve of the sample No. 30.

As above explained with reference to the examples, the magnet alloy according to the invention is comparable with Vicalloy in the magnetic characteristics and workability, but is less expensive than Vicalloy as the magnet alloy according to the invention contains lesser amount of Co and V.

The magnetic characteristics of the magnet alloy according to the invention can be adjusted for a wide range by changing conditions required for components, heat treatments or working processes etc., so that the invention renders it possible to manufacture in an easy manner magnet alloys having magnetic characteristics suitable for a semistationary memory, ferreed or hysteresis motor etc.

We claim:

1. A cold-workable permanent magnet alloy in the form of gamma phase precipitated in a matrix of alpha phase, characterized by a high coercive force of at least about 80 oersteds, consisting essentially of 15 to 42% by weight of Co, 5 to 16% by weight of Ni, the Co and Ni being related to each other by the equation Co wt. percent=(50—2.5 (Ni wt. percent)) to (53—1.5 (Ni wt. percent)), 3 to 9% by weight of Cr, not more than 2% by weight of Mo, not more than 1% by weight of V, not more than 0.1% by weight of C, not more than 1% by weight of Si, not more than 1% by weight of Mn, not more than 1% by weight of Al, and not more than 1% by weight of a member selected from the group consisting of Ti, Nb, Zr and a mixture thereof, balance essentially Fe.

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CHARLES N. LOVELL, Primary Examiner

U.S. Cl. X.R.

75—128 B; 148—31