United States Patent [19]

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[11] **3,836,406**

[45] **Sept. 17, 1974**

[54] **PERMANENT MAGNETIC Fe-Mn-Cr ALLOY CONTAINING NITROGEN**

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[22] Filed: **Dec. 21, 1973**

[21] Appl. No.: **427,361**

Related U.S. Application Data

[63] Continuation of Ser. No. 325,305, Jan. 22, 1973, abandoned, which is a continuation of Ser. No. 60,858, Aug. 7, 1970, abandoned.

[52] **U.S. Cl.** ..... **148/31.57,** 75/126 B, 75/126 J, 75/126 N, 148/121, 75/130.5

[51] **Int. Cl.** **H01f 1/04**

[58] **Field of Search** ..... 75/126 B, 126 J, 126 N, 75/130.5; 148/31.57, 121

[56] **References Cited**

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[57] **ABSTRACT**

A permanent magnetic alloy consists essentially of 0.05 – 0.5 wt. percent N, 5– 15 wt. percent Mn, 2– 12 wt. percent Cr, and remainder iron, produced by solution treatment at a temperature not lower than 900°C, cold rolling to a thickness reduction of 10– 98 percent and if desired, aging at 100° – 800°C.

The alloy may additionally contain Mo, Co, Al, C, Nb, Ti, Zr and V.

1 Claim, 2 Drawing Figures

FIG. 2

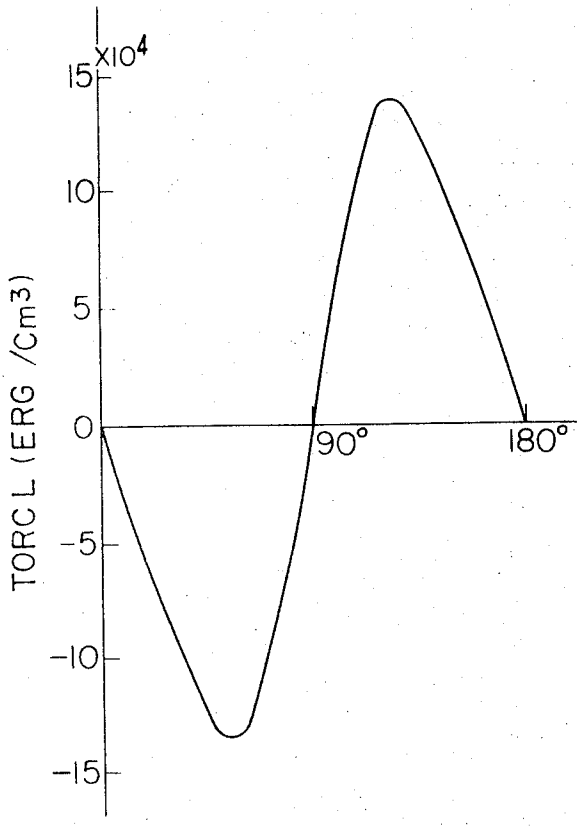
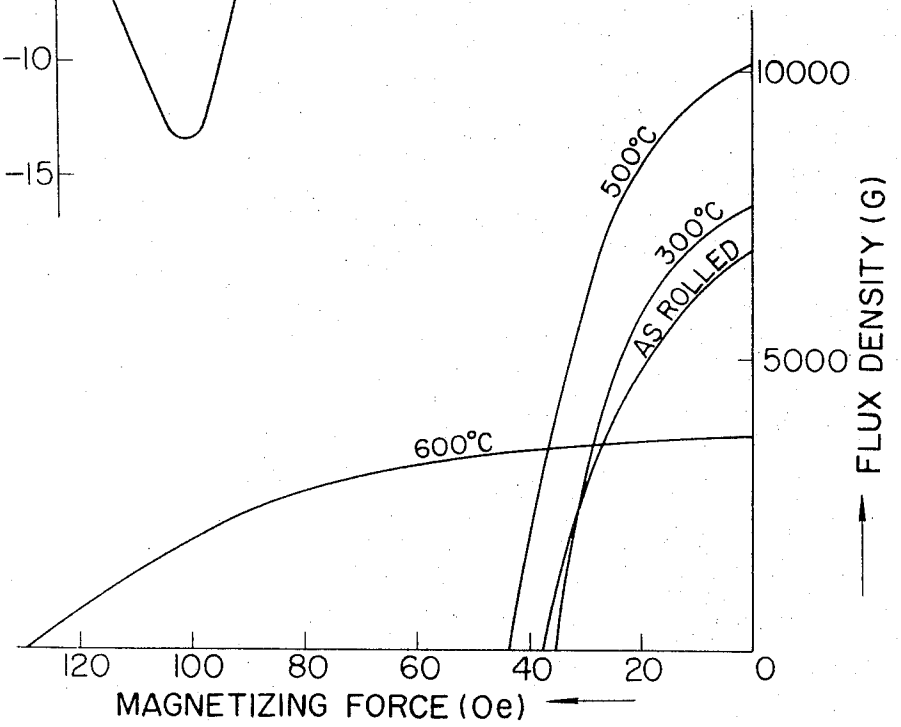

X10⁴
15
10
5
0
-5
-10
-15
TORQUE (ERG /Cm³)
90°
180°

FIG. 1


10000
5000
500°C
300°C
AS ROLLED
600°C
FLUX DENSITY (G)
120
100
80
60
40
20
0
MAGNETIZING FORCE (Oe)

PERMANENT MAGNETIC Fe-Mn-Cr ALLOY CONTAINING NITROGEN

This application is a continuation of application Ser. No. 325,305, filed Jan. 22, 1973, which is a continuation of application Ser. No. 60,858, filed Aug. 7, 1970, both now abandoned.

This invention relates to a permanent magnetic alloy, and more particularly, to a permanent magnetic alloy mainly composed of Fe-Mn-Cr, containing nitrogen, and if desired, at least one of Mo, Co, Al, Nb, Ti, Zr, V and C being added thereto, produced by solution treatment over 900°C, cold rolling, and if desired aging.

The permanent magnetic alloy has excellent permanent magnetic characteristics, high cold rolling property and does not contain expensive elements, and even if they are contained, the amount of them is so small that the cost is very low.

In general, magnetic characteristics of permanent magnet is shown by residual flux density. Br, coercive force Hc, maximum energy product and the like. The higher these values, the stronger the magnet. Representative example is Alnico magnet mainly composed of Fe-Ni-Co-Al-Cu. However, Alnico magnet contains expensive and not easily available elements such as nickel, cobalt and the like. In addition, alnico magnet is disadvantageously so rigid and brittle that neither forging, rolling, lathing nor punching is possible. Only grinding working can be employed. However, it is often requested to use a permanent magnet in a form of thin plate and fine wire and it is desired that a permanent magnet has plastic workability such as bending and press punching.

Sometimes a permanent magnet having relatively low coercive force such as so-called "semi-hard magnet" is required. The permanent magnet according to this invention is very useful for such request.

Heretofore, there have been known "Vicalloy" and "Cunife" which can be cold-rolled to produce wire and thin plate.

Further it is also known that an extensive cold rolling of **18-8** stainless steel containing 18 percent Cr and 8 percent Ni results in revealing of permanent magnet property, and the permanent magnet thus produced has been used as a recording wire material for a wire recorder. However, these alloys also need expensive and not easily available nickel and cobalt in an large amount. Therefore, they are used only in special fields such as special motors, miniature motors and magnetic memory elements.

It is clearly desirable to produce the above-mentioned permanent magnets in a large amount at low cost in view of the recent development of electronic device and automation devices.

Heretofore, an iron alloy containing about 12 percent Mn and 1 to 1.3 percent C (not containing Ni and Co) and having workability, so-called "Hadfield" steel, has been known. This steel is not magnetic at a stage of solution treatment, but becomes ferromagnetic by cold rolling to show permanent magnet property. The magnetic behavior in the cold rolling step is explained as follows. The steel becomes non-magnetic γ-phase by solution treatment from metallographical point of view and the cold rolling converts the phase to α-phase resulting in ferromagnetic property.

Furthermore, such steel containing manganese causes α-transformation at a relatively low degree of working to be hardened so that this steel has been widely used as a material of antiabrasion tool, but hardly used as a magnetic material.

According to this invention, the cold rolling causes γ-α transformation of the Fe-Mn system alloy and further Cr (accelerating α-transformation) and nitrogen (stabilizing γ-phase) are incorporated to the alloy at an appropriate ratio so as to control amount of α-phase produced by cold rolling. Therefore, Br and Hc contributing to permanent magnetic characteristic can be optionally controlled.

An important feature of the alloy of this invention is that nitrogen is used as a component of the alloy though nitrogen has never been used as a component of magnetic material and no advantage of incorporation of nitrogen has never been found. In general, when a metal is molten in air, nitrogen in air is dissolved in the metal, but the amount of nitrogen thus incorporated is only less than 0.1 percent.

Nitrogen is a most important element affecting the characteristics of alloy of this invention. When the nitrogen content is less than 0.05 percent, α-phase amounts to a large content and the cold rolling property is not improved while at a nitrogen content exceeding 0.5 percent the magnetic property is deteriorated. Therefore, nitrogen content ranging from 0.05 to 0.5 percent is selected according to this invention.

When the manganese content is less than 5 percent, a large amount of α-phase is already present after the solution treatment so that the cold rolling property is hardly present while at a manganese content exceeding 15 percent the magnetic property is lowered. Thus, the present invention defines the manganese content as from 5 to 15 percent.

When the chromium content is less than 2 percent, the magnetic property is not remarkably improved by the cold rolling while at a chromium content exceeding 12 percent the cold rolling property is lowered. Therefore, chromium content ranging from 2 to 12 percent is employed in this invention.

The cold rolling is not markedly deteriorated by not more than 4 weight percent molybdenum, not more than 12 weight percent cobalt, not more than 2 weight percent aluminum, not more than 3 weight percent niobium, titanium, zirconium, and vanadium, and these elements added singly or in combination, improve magnetic property. With respect to amounts of these elements and the carbon below, a part of the iron weight percent is replaced by the total weight percent of these elements and carbon added.

With respect to carbon, a carbon content up to 0.4 percent can remarkably improve the cold rolling without deterioration of magnetic property.

According to this invention, magnetic property of the alloy can be controlled by selecting the chemical components and further the α-phase formed by the cold rolling is inversely transformed to γ-phase by the aging treatment so that the amount ratio of α-phase and γ-phase can be optionally controlled by selecting the aging conditions, and the Br can be markedly increased by recrystallization.

According to another aspect of this invention, there is provided a permanent magnetic alloy consisting essentially of from 0.05 to 0.5 weight percent nitrogen, from 5 to 15 weight percent manganese, from 2 to 12

weight percent chromium, and remainder iron, produced by hot working at a temperature not lower than 900°C accompanied with solution treatment, cold rolling resulting in a thickness reduction of 10 to 98 percent, and if desired, aging. Further, this alloy may contain Mo, Co, Al, Nb, Ti, Zr, V and C as previously mentioned.

The hot working is effected at a temperature not lower than 900°C and then quenched to cause a solution treatment effect.

The present invention will be further described referring to the drawing in which:

FIG. **1** shows a demagnetizing curve of permanent magnetic alloy according to this invention; and

FIG. **2** shows a magnetic torc curve of permanent magnetic alloy according to this invention.

Referring to FIG. **1** the demagnetizing curves are those for permanent magnetic alloys composed of 0.227 weight percent nitrogen, 11.11 weight percent Mn, 9.17 weight percent Cr, 2.16 weight percent Mo, 1.18 weight percent Al and remainder iron produced by solution treatment, cold rolling to a thickness reduction of 50 percent and aging treatment at various temperatures. The temperature shown in the graph is a temperature at which the aging treatment is effected. The "AS ROLLED" means the alloy shown by the curve is subjected to solution treatment and cold rolling, but not aging.

The phase formed by cold rolling is reversely transformed to γ-phase by aging. Therefore, the amount ratio of α-phase to γ-phase can be optionally controlled and the Br can be remarkably increased by recrystallization as shown in FIG. **1.**

Referring to FIG. **2,** the magnetic torc is that of permanent magnetic alloy composed of 0.169 weight percent nitrogen, 9.20 weight percent Mn, 8.62 weight percent Cr, 1.62 weight percent Mo, 5.21 weight percent Co and remainder iron, produced by solution treatment, cold rolling to a thickness reduction of 55 percent, and aging at 500°C.

The abscissa of FIG. **2** represents an angle between a cold rolling direction and a magnetizing direction.

As is clear from FIG. **2,** the permanent magnetic alloy has a rolling effect having the magnet easy axis to the direction of rolling.

The following Example is given for illustrating the present invention, but, by no means, should be construed as restricting the present invention.

EXAMPLE

As the starting metal, an electrolytic iron was used, and a nitrided manganese containing 6 percent nitrogen and a nitrogen containing ferrochrome containing 40 percent Cr and 6.5 percent N were employed for adding Mn, Cr as well as N to the electrolytic iron. Carbon was added by using ferro-carbon containing 4 percent C, and as Mo, Co, and Al, each commercially available pure metal is used.

Allous containing various ratio of components were prepared by using a high frequency electric furnace, and an ingot obtained by molding was forged at 1,150°C and then made into a thin plate of 5mm. thick at 1,000°C by hot rolling to prepare samples.

The samples were subjected to a solution treatment by heating at 1,050°C for 30 minutes and cooling with water. And then cold rolling at various working ratio was effected. The samples thus treated were compared with samples which were subjected to aging at 100°C to 900°C for one hour in addition to the above mentioned treatments with respect to Br and Ho by using a automatic recording flux meter.

Representative results are shown below.

1. An alloy composed of 0.222 weight percent nitrogen, 11.03 weight percent Mn, 9.72 weight percent Cr, 2.04 weight percent Mo, and remainder iron was subjected to solution treatment at 1,030°C and then to cold rolling resulting in a thickness reduction of 50 percent. The alloy thus treated has a residual flux density, Br, of 6,700 gauss (G) and a coercive force, HC, of **44** oersteds (Oe).

2. When the above-mentioned alloy was cold rolled to a thickness reduction of 75 percent in place of 50 percent, the alloy thus cold rolled had a residual flux density, Br, of 8,900 G and a coercive force, Hc, of 56 Oe.

3. The alloy obtained in (2) above was subjected to aging at 500°C for 1 hour. The resulting alloy had a residual flux density, Br, of 10,700 G and a coercive force, Hc, of 56 Oe.

4. The alloy obtained in (2) above was subjected to aging at 600°C for 1 hour. The alloy thus aged had a residual flux density, Br, of 2,400 G and a coercive force, Hc, of 160 Oe.

5. An alloy composed of 0.301 weight percent nitrogen, 10.12 weight percent Mn, 9.63 weight percent Cr, 2.10 weight percent Mo and remainder iron was subjected to solution treatment at 1,050°C and then cold rolled to a thickness reduction of 75 percent. The resulting alloy had a residual flux density, Br, of 8,200 G and a coercive force, Hc, of 49 Oe.

6. The alloy obtained in (5) above was subjected to aging at 500°C for 1 hour. The alloy thus aged had a residual flux density, Br, of 12,300 G and a coercive force, Hc, of 60 Oe.

7. An alloy composed of 0.227 weight percent nitrogen, 11.11 weight percent Mn, 9.17 weight percent Cr, 2.10 weight percent Mo, 1.18 weight percent Al and remainder iron was subjected to a solution treatment at 1,050°C, cold rolled to a thickness reduction of 75 percent, and aged at 500°C for 1 hour. The resulting alloy had a residual flux density, Br, of 12,300 G and a coercive force, Hc, of 50 Oe.

8. The starting alloy as used in (7) above was subjected to a similar solution treatment, cold rolled to a thickness reduction of 50 percent, aged at 500°C for 1 hour and then cold rolled again to a thickness reduction of 50 percent. The resulting alloy had a residual flux density, Br, of 10,700 G and a coercive force, Hc, of 68 Oe.

9. An alloy composed of 0.184 weight percent nitrogen, 10.30 weight percent Mn, 9.23 weight percent Cr, 2.10 weight percent Mo, 10.65 weight percent Co, and remainder iron was subjected to a solution treatment at 1,050°C, cold rolled to a thickness reduction of 83.5 percent, and aged at 550°C for 1 hour. The resulting alloy had a residual flux density, Br, of 8,800 G and a coercive force, Hc, of 115 Oe.

10. An alloy composed of 0.189 weight percent nitrogen, 10.50 weight percent Mn, 8.74 weight percent Cr, 1.86 weight percent Mo, 0.14 weight percent C and remainder iron was subjected to a solution treatment at 1,050°C, cold rolled to a thickness reduction of 65 percent, and aged at 500°C for 1 hour. The resulting alloy

had a residual flux density, Br, of 9,800 G and a coercive force, Hc, of 70 Oe.

11. An alloy composed of 0.168 weight percent nitrogen, 6.90 weight percent Mn, 8.67 weight percent Cr and remainder iron was subjected to a solution treatment at 1,050°C and cold rolled to a thickness reduction of 50 percent. The resulting alloy had a residual flux density, Br, of 6,300 G and a coercive force, Hc, of 65 Oe.

In Table 1 below there is shown comparison of an alloy of this invention with conventional Cu-Ni-Fe system alloy and Fe-Ni-Cr system alloy with respect to What is claimed is:

TABLE 1

Alloy	Composition, treatment an processing	Residual flux density Br (gauss)	Coercive force Hc (oersteds)
This invention	Mn 10.12%, Cr 9.63% Mo 2.10%, N 0.3013%; cold rolled to a thickness reduction of 75%; aged at 500°C.	12300	59
Cu-Ni-Fe alloy	Fe 20% Ni 20% Cu 60%; rapidly cooled from 1000°C.	2000	200
do.	The alloy treated as above is aged at 650°C.	3200	400
do.	The alloy having the above composition is cold rolled to a thickness reduction of 95% and aged at 650°C.	5000	440
Fe-Ni-Cr alloy	Ni 18%, 4%; cold rolled to a thickness reduction of 83%.	7000	30
do.	Ni 18%, Cr 8%; cold rolled to a thickness reduction of 93%.	800	178

magnetic characteristics. It is clear from Table 1 that the Fe-Mn-Cr system alloy containing nitrogen according to this invention has excellent characteristics.

1. A heat-treated permanent magnetic alloy article consisting essentially of from about 0.2 to 0.4 weight percent nitrogen, from about 9 to 12 weight percent manganese, from about 8 to 10 weight percent chromium, from about 1 to 3 weight percent molybdenum and the remainder iron, said weights based on the total weight of the article, said article produced by solution treating the alloy at a temperature not lower than about 900°C, cold rolling the treated alloy to a thickness reduction from about 50 to 75 percent and thereafter aging the alloy at a temperature from about 300° to 500°C, said alloy having a residual flux density of at least 9,000 gauss and exhibiting a coercive force less than about 100 oersteads.

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