May 1, 1973 HIROSHI YAMAMOTO 3,730,784
METHOD OF MAKING MAGANESE-ALUMINUM-CARBON
TERNARY ALLOYS FOR PERMANENT MAGNETS
Original Filed Feb. 1, 1965 3 Sheets-Sheet 1

FIG. 1

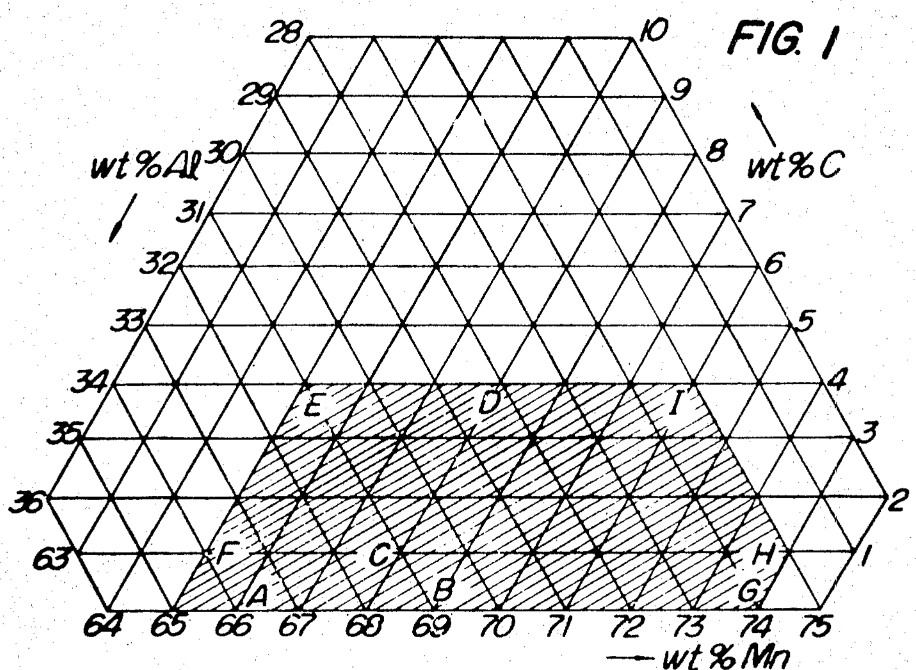
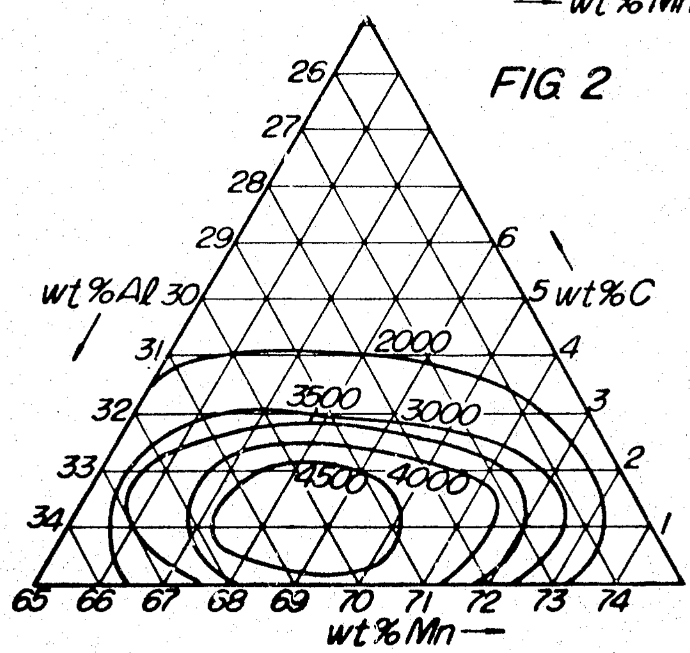
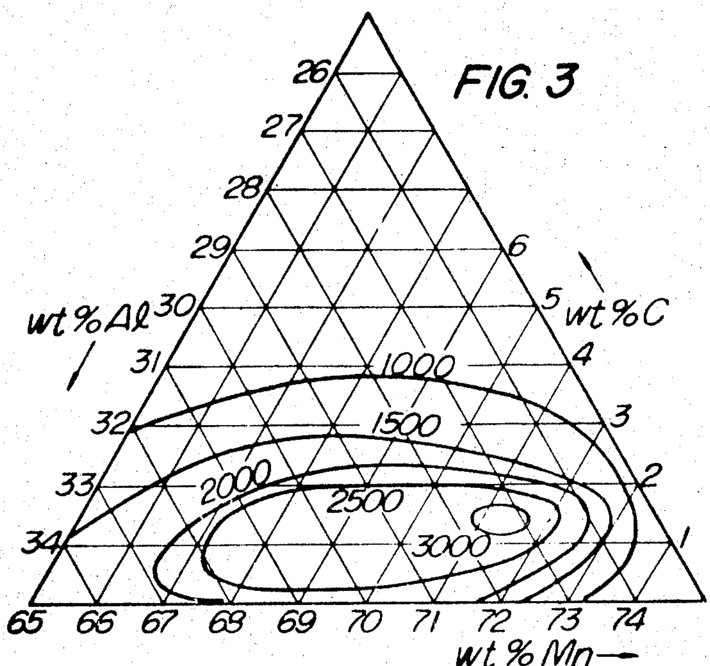


FIG. 2

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wt % Al
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74
wt % Mn

FIG. 3

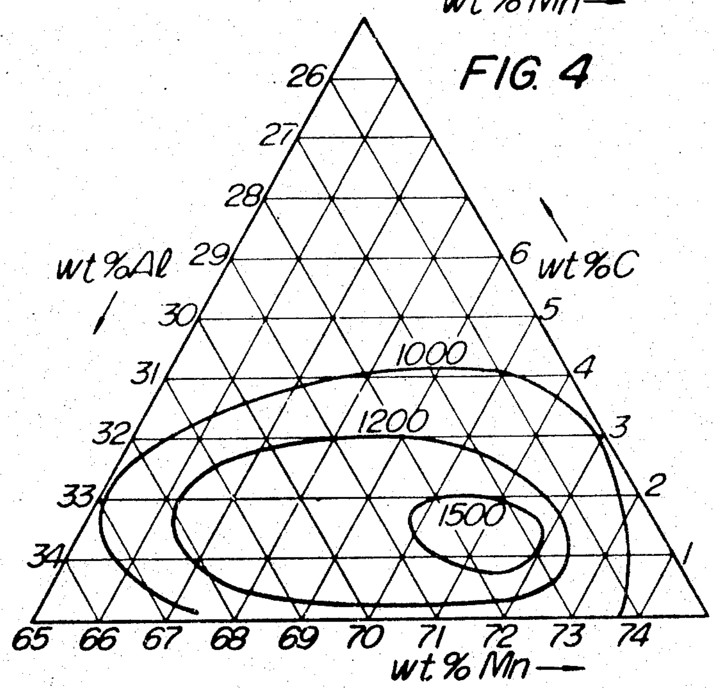
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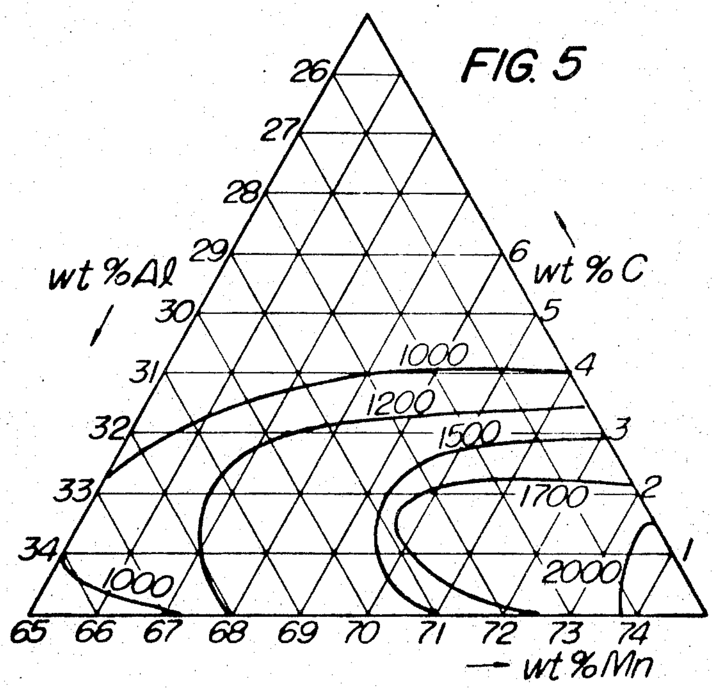
FIG. 4

FIG. 5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66
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71
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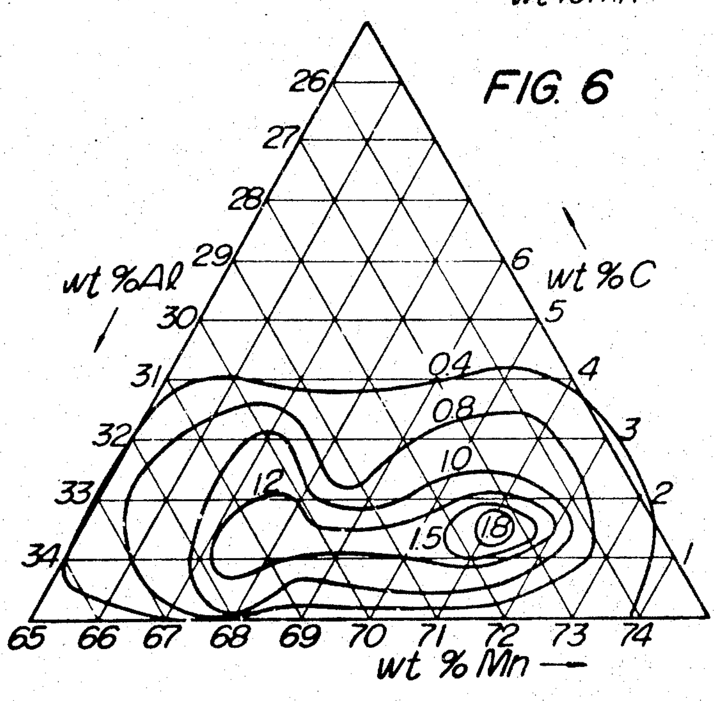
wt %Mn

FIG. 6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1.5
1.8
65
66
67
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69
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71
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73
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wt %Mn

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3,730,784

METHOD OF MAKING MANGANESE-ALUMINUM-CARBON TERNARY ALLOYS FOR PERMANENT MAGNETS

Hiroshi Yamamoto, Osaka, Japan, assignor to Matsushita Electric Industrial Co., Ltd., Kadoma-shi, Osaka, Japan

Continuation of application Ser. No. 429,260, Feb. 1, 1965. This application July 28, 1969, Ser. No. 850,307
Claims priority, application Japan, Feb. 1, 1964, 39/5,653; Mar. 3, 1964, 39/12,679
Int. Cl. H01f *1/04*
U.S. Cl. 148—101 10 Claims

ABSTRACT OF THE DISCLOSURE

Ternary alloys consisting essentially of, by weight, (a) 67 to 69% Mn, 29 to 32.0% Al, and 0.3 to 3.0% C, and (b) 70.0 to 72.5% Mn, 26.5 to 29.0% Al and 0.5 to 2.5% C, are prepared by heating the selected alloy composition to a temperature of about 1380° C. to form a melt, casting the melt in a mold to form an ingot, quenching the ingot from a temperature of 880° to 1250° C. and then isothermally tempering the quenched ingot at a temperature of 380° to 700° C. The thus heat-treated alloys are suitable for use as permanent magnets with magnetic properties superior to those of binary alloys of similar manganese and aluminum contents.

This application is a continuation of copending application Ser. No. 429,260, filed Feb. 1, 1965, and now abandoned..

The present invention relates to an entirely novel material for permanent magnets and more particularly to manganese-aluminum-carbon ternary alloys in which a suitable amount of carbon is added positively as a new and third element to the already known magnetic material of manganese-aluminum binary alloys.

The primary object of the present invention is to provide a method for making manganese-aluminum-carbon ternary alloys for permanent magnets, whose residual induction Br, coercive force H_c, maximum energy product BH_{max}, saturation magnetization $4\pi I_s$ and others, are higher than those of the prior magnetic materials of manganese-aluminum binary alloys.

According to a prior method for obtaining permanent magnets of manganese-aluminum binary alloys, when an alloy consisting of about 72% by weight manganese and about 28% by weight aluminum is subjected to a suitable heat treatment, it transforms from the high temperature hexagonal epsilon phase to tetragonal metastable phase. The manganese-aluminum alloys thus subjected to the transformation become ferromagnetic, but their magnetic properties in respect of, for example, BH_{max} is quite poor or only of the order of 0.6×10^6 G·oe. Therefore, it has been difficult to use the manganese-aluminum binary alloys for practical application as permanent magnets.

The inventors have discovered that alloys in which carbon is added purposely as a third element to such manganese-aluminum alloys are so excellent that they have improved magnetic properties, have a high antioxidation property, have a widened composition range showing excellent magnetic properties and can be subjected to heat treatments under conditions which are not so severe as compared with prior conditions.

According to the present invention, there is also provided a method for making manganese-aluminum-carbon ternary alloys for extremely powerful permanent magnets, comprising the steps of preparing a mixture essentially consisting of from 67.0 to 69.0% by weight metallic manganese, from 29.0 to 32.0% by weight metallic aluminum and from 0.3 to 3% by weight carbon, or consisting of from 70.0 to 72.5% by weight metallic Mn, from 26.5 to 29.0% by weight Al and from 0.5 to 2.5% by weight C, heating to melt the mixture at a temperature range of 1260° to 1500° C. in at least one atmosphere selected from the atmosphere group of inert gas, reducing gas and vacuum, casting the melt into a mold to obtain an ingot, quenching the ingot from a temperature range of 880° to 1250° C., and then tempering the ingot at a temperature range of 380° to 760° for a predetermined time.

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Other objects and particularities of the present invention will become more obvious as the description proceeds.

In the accompanying drawings:

FIG. 1 is a composition diagram of manganese-aluminum-carbon ternary system in which the portion surrounded by thick line shows a preferred composition range of the alloys according to the present invention; and

FIGS. 2 to 6 are graphic representations of equivalent curves of saturation magnetization $4\pi I_s$, residual induction Br, coercive force Hc, intrinsic coercive force $_I$Hc, and maximum energy product BH_{max} of the inventive alloys as drawn on the composition diagram thereof, respectively.

Metallic manganese, metallic aluminum and carbon are weighed in various percentages to obtain mixtures of the three elements of various compositions. The mixtures are charged into respective crucibles and are heated to melt in one or more of atmospheres selected from the group of inert gas, reducing gas and vacuum. Melting temperatures for the mixtures vary depending on their compositions, but lie within a range of 1260° to 1500° C. Preferred melting temperature is about 1380° C. and at this temperature the three elements are effectively alloyed. It is preferred that the mixtures are heated up to about 800° C. in a vacuum and in a temperature range thereabove heated in an argon atmosphere. Then the melts are cast into suitable molds or are cooled in the crucibles to obtain ingots of predetermined size. In order to homogenize the alloys, the ingots may be subjected to forging, solution treatment or any other treatment, but this step is not necessarily required..

Table 1 below shows chemical compositions, as determined by chemical analysis, of thirty-three specimens selected from the ingots of the manganese-aluminum-carbon ternary alloys thus obtained. FIG. 1 shows a composition diagram of the manganese-aluminum-carbon ternary alloys which are included in the composition range within the line A-G-H-I-E-F.

TABLE 1

Specimen number	Percent by weight		
	Mn	Al	C
1	69.2	30.5	0.3
2	70.0	29.6	0.4
3	71.4	28.0	0.6
4	71.8	27.4	0.8
5	72.5	26.5	1.0
6	73.5	25.5	1.0
7	69.0	28.1	2.9
8	68.4	29.3	2.3
9	69.5	27.5	3.0
10	70.2	28.3	1.5
11	70.8	27.8	1.4
12	71.2	27.2	1.6
13	72.1	26.3	1.6
14	70.5	26.4	3.1
15	70.3	25.7	4.0
16	71.6	25.0	3.4
17	69.0	26.5	4.5
18	72.5	24.5	3.0
19	73.7	26.2	0.1
20	72.1	27.9	0.02
21	67.9	31.8	0.3
22	66.0	33.7	0.3
23	65.1	34.0	0.9
24	67.3	31.6	1.1
25	68.9	31.0	0.1

TABLE I—Continued

Specimen number	Percent by weight		
	Mn	Al	C
26	67.8	30.3	1.9
27	65.2	32.5	2.3
28	64.5	33.5	2.0
29	67.0	30.1	2.9
30	65.3	31.0	3.7
31	64.8	31.0	4.2
32	67.4	28.6	4.0
33	66.6	29.0	4.4

Some of these alloys show ferromagnetic properties as they are molten and as cast. No. 4 specimen, for example, has magnetic properties of the order of Br.=2000 G, Hc=500 oe. and $BH_{max}=0.4\times10^6$ G·oe. Since however these values are still insufficient for a permanent magnet, all the specimens are subjected to the following heat treatments. In a first step, the specimens are subjected to water or oil quenching from a temperature of 1100° C. The quenching temperature may desirably suitably be varied depending on the alloy compositions, but a quenching temperature range of 880° C. to 1250° C. is sufficient. Then, the quenched alloys are subjected to a second heat treatment or isothermal tempering in a temperature range of 380° C. to 760° C. for a suitable time of the order of from several minutes to several hundred hours. By these heat treatments, those alloys which did not show any ferromagnetic properties as they were cast become ferromagnetic, and those which already showed ferromagnetic properties as they cast show further improved magnetic properties.

The purpose of the two heat treatments is to cause in the ternary alloys the transformation similar to that caused in the manganese-aluminum binary alloys. But the difference between there is that, in the ternary alloys of the present invention including therein carbon, allowable ranges of temperature and time in both of the first step and the second step heat treatments are far wider than in the case of the binary alloys. Temperature and time settings for the second heat treatment vary depending on the alloy composition, and magnetic properties obtained also greatly vary by a combination of temperature and time. Conditions for obtaining best magnetic properties with respect to the respective alloys are not common to all cases. Though it is difficult to set up comprehensive conditions for all of the ternary alloys, the optimum conditions may, for example, be such as are shown in Table 2. As seen from Table 2, the tempering temperature for the ternary alloys is 500° to 650° C., preferably.

TABLE 2

Specimen number	Temperature (° C.)	Time (hr.)
1	600	1
2	600	1.5
3	600	3
4	600	3
5	630	2
6	650	3
7	600	1.5
8	600	1.5
9	600	2
10	600	1.5
11	600	1.5
12	600	1.5
13	630	2
14	630	2
15	650	2
16	650	2
17		
18		
19	650	3
20	600	1
21	500	6
22	500	4
23	500	4
24	550	3
25	600	1
26	550	3
27	500	6
28		
29	600	1.5
30	550	4
31		
32	600	3
33		

It will be seen from the above table that No. 3 alloy, for example, shows best magnetic properties when tempered for 3 hours at 600° C. or for 8 hours at 540° C. In case of No. 21 alloy, it shows a maximum energy product BH_{max} of 1.05×10^6 G·oe. when quenched from 1150° C. and tempered for 6 hours at 500° C., and shows a maximum energy product BH_{max} of the same value when tempered for 35 minutes at 620° C. No. 21 alloy however shows poor magnetic properties when tempered for 35 minutes at 500° C. and it has a poor BH_{max} value of 0.4×10^6 G·oe. Even when tempered for 6 hours at 500° C., No. 29 alloy shows a poor BH_{max} value of 0.2×10^6 G·oe. The just-mentioned alloy however shows a high BH_{max} value of $1.18\times10.^6$ G·oe. under different heat treatment conditions. In General, it seems that best results can be obtained at a higher tempering temperature and a longer time in case of the manganese rich alloys and at a lower tempering temperature and a shorter time in case of the manganese poor alloys.

As described above, there are optimum tempering temperature and time for each of said alloy compositions, and it is difficult to set up definite temperature and time settings common to all of the alloy compositions. Therfore, it is to be understood that magnetic properties of the alloys of various compositions hereunder described represent the values when each alloy is subjected to a heat treatment by which it shows the most excellent properties.

Magnetic properties of the ternary alloys are as tabulated in Table 3 and, when shown in the form of equivalent curves on the ternary composition diagram are as depicted in FIGS. 2 to 6.

TABLE 3

Specimen Number	$4\pi Is$ (G)	Br (G)	Hc (oe.)	$_IHc$ (oe.)	$BH_{max.}$ ($\times10^6$ G·oe.)
1	5,000	2,700	1,100	1,300	0.82
2	4,700	2,500	1,250	1,450	1.00
3	4,100	2,500	1,400	1,700	1.18
4	3,800	2,450	1,500	1,750	1.18
5	3,100	2,050	1,300	1,800	0.91
6	1,800	1,000	800	2,100	0.53
7	2,700	1,350	1,000	1,100	0.72
8	4,300	1,700	750	1,050	0.51
9	2,500	1,400	1,200	1,300	0.82
10	4,300	2,650	1,650	1,750	1.30
11	4,000	2,900	1,800	1,850	1.78
12	4,100	3,000	1,800	1,850	1.83
13	3,100	2,000	1,200	1,800	1.09
14	2,500	1,450	1,100	1,600	0.87
15	1,150	900	1,050	1,200	0.42
16	1,100	850	1,100	1,250	0.40
17	Non-magnetic				
18	Non-magnetic				
19	1,150	900	1,100	2,050	0.61
20	3,200	1,500	1,000	1,500	0.51
21	4,300	2,600	1,250	1,400	1.05
22	2,900	1,800	600	900	0.40
23	2,900	1,900	750	1,000	0.60
24	4,600	2,700	1,250	1,300	1.26
25	4,400	2,400	1,200	1,400	0.80
26	4,700	2,550	1,200	1,250	1.21
27	2,800	1,300	1,050	1,150	0.80
28	Nonmagnetic				
29	3,400	1,750	1,200	1,300	1.18
30	2,100	950	850	1,000	0.42
31	Non-magnetic				
32	2,050	900	800	850	0.32
33	Non-magnetic				

From the above table, it can roughly be concluded that the alloys having a low manganese content have high values of 4π Is and Br and low values of Hc and $_IHc$, while those having a high manganese content have low values of 4π Is and Br and high values of Hc and $_IHC$. However, values of BH_{max} obtained by a relation between Br and Hc show fluctuation of extremely complicated nature and it is impossible to find out a definite tendency thereof. Roughly, those alloy compositions including about 1 to 2% by weight carbon show good magnetic properties. In this case too, excellency of the magnetic properties is greatly influenced by the amount of maganese and aluminum. As far as BH_{max} is concerned, it seems that BH_{max} is greatly influenced by the percentages of manganese, aluminum and carbon in the ternary alloys. Those alloys falling within a composition range of from 67 to 69% by weight manganese, from

29 to 32% by weight aluminum and from 0.3 to 3.0% by weight carbon and a composition range of from 70 to 72.5% by weight manganese, from 26.5 to 29% by weight aluminum and from 0.5 to 2.5% by weight carbon show especially excellent magnetic properties and they have a BH_{max} value of $BH_{max} \geqq 1.0 \times 10^6$ G·oe.

Some of the manganese-aluminum-carbon ternary alloys consisting of from 65.0 to 69.0% by weight manganese, from 31.0 to 34.0% by weight aluminum, and less than 1.0% by weight carbon, that is, the alloys having a composition falling within a portion surrounded by the line A-B-C-F in FIG. 1, have a BH_{max} value of the order of 1.05×10^6 G·oe. Some of the manganese-aluminum-carbon ternary alloys consisting of from 65.0 to 68.0% by weight manganese, from 28.0 to 34.0% by weight aluminum and from 1.0 to 4.0% by weight carbon, that is, the alloys having a composition falling within a portion surrounded by the line C-D-E-F, have a BH_{max} value of the order of 1.26×10^6 G·oe. Further, some of the manganese-aluminum-carbon ternary alloys consisting of from 68.0 to 74.0% by weight manganese, from 25.0 to 31.0% by weight aluminum and less than 4.0% by weight carbon, that is, the alloys having a composition falling within a portion surrounded by the line B-G-H-I-D-C, have a BH_{max} value of the order of 1.83×10^6 G·oe.

From the foregoing description, it will be known that the manganese-aluminum-carbon ternary alloys according to the present invention have a very wide composition range in which they show a BH_{max} value of $BH_{max} \geqq 1.0 \times 10^6$ G·oe. In contrast, the manganese-aluminum binary alloys which generally have a BH_{max} value of the order of 0.5 to 0.6×10^6 G·oe., have a narrow composition range showing ferromagnetic properties and have a narrow allowable range of heat treatment for the purpose of obtaining ferromagnetic properties. It is quite apparent from the above experiments that the alloys obtained by the above-mentioned process provide a BH_{max} value of the order of $BH_{max} \geqq 0.5 \times 10^6$ G·oe. over a wide composition range of from 65.0 to 74.0% by weight manganese, from 25.0 to 34.0% by weight aluminum and less than 4.0% by weight carbon, and can be heat-treated under conditions which are not so severe compared with the manganese-aluminum binary alloys. Thus, it will be understood that the addition of carbon exhibits such a great effect.

Carbon may be added in any amount less than 4.0% by weight excluding zero since addition of carbon in a very small amount, for example, 0.02% by weight can effectively improve the magnetic properties. Further, the magnetic properties of the inventive alloy would not be affected by the inclusion therein of impurity elements, other than manganese, aluminum and carbon, which may commonly be found in ordinary alloys. No variation in the magnetic properties was observed even with inclusion of certain impurity elements in an amount up to 2% by weight.

What is claimed is:

1. A method of making manganese-aluminum-carbon

ternary alloys for a permanent magnet, comprising the steps of (1) selecting an alloy composition which consists essentially of (a) 67.0 to 69.0% manganese by weight, 29.0 to 32.0% aluminum by weight and 0.3 to 3.0% carbon by weight or (b) 70.0 to 72.5% manganese by weight, 26.5 to 29.0% aluminum by weight and 0.5 to 2.5% carbon by weight, (2) heating the selected alloy composition at a temperature of about 1380° C. to form a melt, (3) casting the melt into a mold to obtain an ingot, (4) quenching the ingot from a temperature of 880° to 1250° C., and (5) then isothermal tempering the ingot at a temperature of 380° to 760° C.

2. The method according to claim 1 in which the alloy composition consists essentially of 67.0 to 69.0% manganese by weight, 29 to 32% aluminum by weight and 0.3 to 3% carbon by weight.

3. The method according to claim 1 in which the alloy composition consists essentially of 70.0 to 72.5% manganese by weight, 26.5 to 29.0% aluminum by weight and 0.5 to 2.5% carbon by weight.

4. The method according to claim 1 in which heating step (2) is carried out in an atmosphere selected from the group consisting of an inert gas, a reducing gas and a vacuum.

5. The method according to claim 1 wherein tempering step (4) is carried out for a period of 1.0 to 6.0 hours.

6. The method according to claim 1 in which heating step (2) is carried out in two stages, first under vacuum from room temperature to about 800° C., then in an argon atmosphere to a temperature of about 1380° C.

7. The method according to claim 1 in which the ingot is quenched in oil.

8. The method according to claim 1 in which the ingot is quenched in water.

9. The method according to claim 2 in which the ingot is quenched from a temperature of 1100° C. in step (3) and the quenched ingot is then tempered at a temperature of 500° to 650° C. in step (4).

10. The method according to claim 3 in which the ingot is quenched from a temperature of about 1100° C. in step (3) and the quenched ingot is then tempered at a temperature of 500° to 650° C. in step (4).

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L. DEWAYNE RUTLEDGE, Primary Examiner
G. K. WHITE, Assistant Examiner

U.S. Cl. X.R.

148—31.57, 102; 75—134 M