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PERMANENT MAGNET

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The present invention relates to permanent magnets and the production thereof from an alloy capable of improvement by precipitation hardening.

It is known that alloys having an iron-nickel-aluminium base and containing, for example from 20% to 30% nickel and from 10% to 14% aluminium constitute high-grade permanent magnet materials, the magnetic characteristics of which can be improved by the addition of cobalt, copper and titanium with a simultaneous reduction of the nickel and aluminium content. It is also known in the art to give a preferred magnetic position in one direction or plane to corresponding iron alloys containing less than 20% nickel and more than 12% cobalt by cooling from about 1,200° C., in a strong magnetic field of maximum homogeneity, the permanent magnetic properties of the alloys simultaneously undergoing a considerable increase. In all these alloys, it is a generally accepted rule that the magnetic properties are impaired above all by contents of silicon, as in the case of contents of manganese, chromium, vanadium, antimony, tin and sulphur, so that in the production of these alloys the greatest value is generally attached in practice to keeping as low as possible the silicon contents which may arise from the raw materials, the scrap introduced and the crucible material introduced by calcination.

The invention relates to the application of the new discovery that a specially selected silicon content exactly adapted to the cobalt, aluminium and titanium content produces, in contrast to what has hitherto been thought, a considerable improvement in the magnetic properties of iron-nickel - aluminium - cobalt - copper-(titanium) - permanent magnet alloys.

The permanent magnet alloys here concerned are those having contents of from 12% to 30% cobalt, 9% to 26% nickel and 0% to 8% copper, but the alloy range is subject to the limitation that the sum of the nickel content plus one half the cobalt content plus one half the copper content must lie between 24% and 36%. The aluminium, titanium and silicon contents of the alloy are limited by the boundary values of 5.5% to 10% aluminium, 0% to 7% titanium and 0.3% to 2.0% silicon and further by the fact that the weight ratio of silicon to aluminium must lie between 1:20 and 1:4, that of silicon to titanium above 1:10 and that of titanium to aluminium below 1:1. Finally, the aluminium, titanium and silicon contents of the alloy are so adjusted to the cobalt, nickel and copper contents of the

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alloy that the following relation applies, viz., aluminium plus 1.2 silicon plus 0.4 titanium plus or minus a maximum of 1.2=0.31 (nickel plus 0.5 cobalt plus 0.5 copper). The contents of these elements in the alloys should here be inserted in percentage by weight for the chemical signs in each case.

Alloys of the type specified are distinguished by particularly favourable values of remanence B_r and of coercivity H_c with simultaneously high values of the maximum energy product BH_{max}, and are therefore pre-eminently suitable for the production of permanent magnets. This discovery is surprising because the coercivity is generally considerably reduced precisely by the addition of silicon or iron, iron-aluminium alloys or iron-nickel-cobalt alloys. The improvement produced in accordance with the invention in the magnetic values of iron-cobalt-nickel-copper-aluminium-titanium permanent magnet alloys within the aforesaid range of composition could therefore by no means be foreseen from the existing state of the art, especially as no effect or further precipitation-hardening was to be expected by the silicon addition. Comparison with the corresponding alloys containing no silicon shows that the addition of silicon produces above all an increase in the remanence and in the maximum energy product $(B \times H)_{max}$, such as could hitherto be obtained only by substantially increasing the cobalt content. Thus, for example, 5% to 10% cobalt can be replaced by an addition of 1% silicon, whereby the cost of the alloy can be considerably lowered. An increase in the coercivity can also be observed with a simultaneous increase in remanence. For example, two to three times the quantity of titanium can also be saved by the addition of silicon and a further reduction in the cost of production thereby effected. The only condition to be observed in replacing a portion of the expensive alloy elements cobalt and titanium is that the above-specified rule as to the mutual dependence of the aluminium, silicon, titanium, nickel and copper contents should be followed as closely as possible. Particularly favourable values can be obtained if the aforesaid tolerance of plus/minus 1.2 is reduced, for example to plus/minus 0.5 or plus/minus 0.3.

In order to promote high coercivity with a relatively low cobalt content, the alloy is preferably employed with a 20% to 26% nickel content.

By way of example, the following two alloys are compared, which were fused in the high-frequency furnace under equal conditions, heat-

treated in the usual manner and measured by the same method:

	Alloy I	Alloy II
Percent C	0.03	0.03.
Percent Ni	18.3	18.6.
Percent Co	19.3	19.5.
Percent Cu	4.0	4.1.
Percent Al	8.1	7.4.
Percent Ti	4.1	4.1.
Percent Si	0.15	0.75.
Percent Fe	Remainder	Remainder.
B_r	6500	7200 Gauss.
H_c	810	835 Oersted.
BH_{max}	$1.9 \cdot 10^6$	$2.3 \cdot 10^6$ Gauss×Oersted.

Alloy II according to the invention thus shows, as compared with the practically silicon-free Alloy I, an improvement in remanence of 10% and in maximum energy product $(B \times H)_{max}$, by which the quality of permanent magnets is principally characterised, even of about 20%. Both alloys were cooled in compressed air from about 1200° C., and thereafter annealed for 1½ hours at 650° C., and for 3 hours at 540° C. On longer annealing, a coercivity of 942 Oersted was even obtained in the case of Alloy II with a remanence of 6600 Gauss, together with a maximum energy product of 2.3×10^6 Gauss×Oersted, that is, an improvement in coercivity of about 16%.

The reduction of the cobalt and/or titanium content which is made possible by the silicon addition appears particularly clearly from the following comparison of two alloys practically free from silicon and two silicon-containing alloys according to the invention.

	Alloy III	Alloy IV	Alloy V	Alloy VI
Percent C		0.03	0.03	0.04.
Percent Ni	18	18.5	16.6	19.3.
Percent Co	35	26.5	26.7	21.7.
Percent Cu			2.4	3.3.
Percent Al	6	7.2	6.0	6.9.
Percent Ti	8	6.8	5.6	4.3.
Percent Si	0.2	0.2	1.3	1.0.
Percent Fe	Remainder	Remainder	Remainder	Remainder.
B_r	5800	5800	6900	6850.
H_c	950	970	970	985.
BH_{max}	1.5	$1.8 \cdot 10^6$	$2.5 \cdot 10^6$	$2.55 \cdot 10^6$.

Remainder iron in this specification and the claims hereof means iron with the usual impurities.

In the case of Alloy III, the composition and magnetic properties of the alloy of this type commercially obtainable in the United States of America have been given in the above table. Alloy IV exhibits, as compared therewith a composition usual in Germany, which allows of obtaining substantially corresponding values. With increased silicon content, on the other hand, an exceptional increase in the remanence and in the BH_{max} product is obtained, as will be seen from the values for the Alloys V and VI. In the case of Alloy V, the titanium content and the aluminium content have at the same time been lowered by the nominal amount of the silicon addition. In the case of Alloy VI there corresponds to an 0.8% increase of the silicon content as compared with Alloys IV a lowering of the titanium content by 2.5%, that is to say, by about three times the quantity by weight. This in itself reduces the cost of the alloy. At the same time, however, the cobalt content of Alloy VI can be lowered by 4.8% as compared with Alloy IV, that is to say, six times the quantity of cobalt are saved in addition by the silicon addition, while the small increase in the nickel and copper content only has a small effect on

cost. This substantial saving of alloy is a result of the surprising improvement of the remanence and of the BH_{max} product shown by the above numerical values.

Particularly favourable values were obtained with the following Alloy VI:

Alloy VII

0.02% C
16.8% Ni
25.0% Co
2.5% Cu
6.4% Al
5.6% Ti
0.65% Si
Remainder Fe

B_r=7250 Gauss
H_c=1010 Oersted
$BH_{max} = 2.84 \cdot 10^6$

As compared with Alloy IV, the additional silicon content here at the same time replaces 2½ times the quantity of titanium and 4 times the quantity of cobalt. With regard to the BH_{max} product of this Alloy VII, it must be noted that this value even exceeds by about 25%, for the isotropic alloy, the upper limit of 2.2 to $2.3 \cdot 10^6$ Gauss×Oersted which has hitherto been stated in technical literature as attainable in practice in aluminium-nickel-cobalt-copper-titanium alloys, obviously without the new maximum value possible with a silicon addition being reached, since in view of the large number of variables a large number of alloy compositions can be found by simple experiment.

Moreover, by means of the alloying steps according to the invention the mechanical properties of the alloys which are important for working up can be favourably influenced owing to the fact that the total quantity of the alloy contents is small, especially the titanium content; thus, for example, the brittleness of these materials is reduced. It naturally lies within the scope of the invention, for the purpose of further favourably influencing these properties which are less characteristic of permanent magnet materials, to provide in addition to the usual impurities formed by the raw materials, key alloys and the crucible material introduced, certain minor alloy additions of one or more of the elements carbon, manganese, phosphorous, sulphur, chromium, vanadium, tantalum, niobium, zirconium, cerium, calcium, antimony, zinc or tin. However, these should not exceed 2% in all and need not be taken into consideration when using the aforesaid rule governing the preparation of the alloy, as the tolerances stated take account thereof.

The aforesaid favourable influence of an increased silicon content in the case of iron-nickel-cobalt-copper-aluminium permanent magnet alloys with and without titanium content, which however, is also dependent upon conformance to the aforesaid rule, naturally has a very marked effect in magnets which are given a preferred magnetic direction in the direction of the magnetic field applied or a corresponding preferred magnetic plane by heat treatment in the magnetic field. In this respect, the reduction of the necesary titanium content produces a particular increase in the Curie point of the alloys and consequently greater susceptibility to the influence of the magnetic field applied.

Thus, in the aforesaid Alloy II according to the invention the following values were measured after cooling from 1200° C., in a homogeneous magnetic field of about 2500 Oersted and subsequent annealing treatment at 650° C., and 540° C.:

B_r=7800 Gauss
H_c=960 Oersted
$BH_{max} = 2.95 - 10^6$ Gauss×Oersted

while in the case of Alloy I practically no increase could be observed on treatment in the magnetic field. The values obtained in the preferred direction in the case of Alloy II could hitherto be obtained only in alloys practically free of silicon and having a cobalt content of from 26% to 30%, from which the advance achieved by the invention is particularly clearly apparent.

A titanium-free Alloy VIII according to the invention will be referred to as a further example:

Alloy VIII

0.02% C
0.2% Mn
1.15% Si
22.9% Ni
14.5% Co
4.0% Cu
Remainder Fe

(*a*) P_r=6900 Gauss
H_c=755 Oersted
BH_{max}=2.05.10^6 Gauss×Oersted
(*b*) P_r=8300 Gauss
H_c=760 Oersted
BH_{max}=2.82.10^6 Gauss×Oersted

The values under (*a*) here apply to the isotropic heat-treated alloy, while those given under (*b*) were measured in the preferred direction after heat treatment in the magnetic field and annealing treatment. It should here be emphasized that comparatively high values of coercivity with correspondingly high values of remanence and of the maximum energy product BH_{max} were not considered to be at all possible in the practically silicon-free alloys produced in the usual manner, without any titanium content and with such a low cobalt content. The steps according to the invention consequently afford a substantial saving of costly alloy metals and at the same time give improved magnetic and mechanical properties.

It has been found expedient to leave the alloys according to the invention in the usual manner below the Curie temperature in the magnetic field in the cooling from temperatures above the Curie point to temperatures about 180° C. below it, in order to obtain as pronounced as possible a preferred magnetic position. It has also been found advantageous to subject the magnets produced from the alloy one or more times to a two-stage annealing treatment below 700° C., for several hours after the magnetic field treatment or after the homogenizing heat treatment without application of a magnetic field. In the described examples of Alloys I to VIII, an annealing treatment of one to two hours was in practice carried out at 650° C., and was followed by an annealing treatment of three to eight hours at 540° C., in accordance with experience, which shows, also with practically silicon-free permanent magnet alloys of the range of composition referred to, that a second annealing treatment at a temperature below 560° C., has a favourable effect on the magnetic properties. It is naturally possible to carry out the second annealing treatment immediately after the first and to obtain the same technical effect by correspondingly slow cooling of the magnets in the furnace within the temperature range of 560° to 480° C., after the completion of the first annealing treatment.

The numerical values given were measured on magnets having an oxidised surface, which were therefore not re-polished after the heat treatment and consequently generally have an austenitic edge layer by which the permanent magnetic properties are known to be reduced. For comparison with specimens polished on all sides, therefore, the above numerical values must be raised by about 10%.

Alloys having an iron-nickel-aluminium-cobalt-(copper)-titanium base are known, which

sometimes have higher BH_{max} values. The silicon-containing alloys to be employed in accordance with the invention differ from such alloys in that they have at equal or lower BH_{max} values far higher stability with respect to extraneous fields, which arises out of the substantially higher coercivity, and in that, as mentioned, the necessary high coercivity values are obtained with lower nickel, cobalt, copper and titanium contents than in the case of alloys practically free from silicon. They are therefore particularly economical and excellently suited for fields of application in which a high permanent accuracy must be ensured. On the other hand, owing to their high coercivity they represent, for example, an ideal material for the manufacture of compressed magnets from mechanically reduced material with an addition of binding agents.

The production of the described alloys can be carried out either by melting or by sintering, the proposed silicon content also having an advantageous effect in the latter case. In this case, the silicon content can conveniently be introduced into the powder mixture to be sintered through the key alloy of high aluminium content which is normally employed, or the relatively expensive pure iron powder, for example carbonyl iron, may conveniently be partially replaced by a further iron key alloy having contents of 4% to 30% (aluminium plus silicon), for example with 6% aluminium and 10% silicon, which can be crushed extremely readily.

It is further advantageous to employ as a quantitative constituent in the production of high-grade sintered magnets a proportion of cast permanent magnet material formed by the silicon-containing alloy according to the invention, which is distinguished by special grain fineness according to the alloy content.

It has also been found that an undeniable operational advantage is achieved due to the fact that in the production of the alloys according to the invention, a substantially silicon-free ferro-titanium is no longer required, as hitherto but a ferro-titanium containing from 35% to 45% titanium, from 5% to 10% silicon and from 6% to 10% aluminium may be employed.

Furthermore, extremely great importance attaches to the fact that the alloys of high titanium content according to the invention can be melted in a furnace having an acid lining, more especially in a high-frequency furnace. As is known the acid crucible lining is considerably less sensitive than a basic lining, which has a great tendency to crack and thus readily leads to perforation of the furnace and to destruction of the coils and of the furnace. The melt taking up solicon which is unavoidable with an acid lining as a matter of fact has a favourable effect in the alloys according to the invention and is taken into account from the outset when determining the composition of the alloy. Thus operational advantages, lower melting costs, a longer life of the furnace and increased operational reliability are simultaneously afforded.

What I claim is:

1. Permanent magnet made from an alloy consisting of:

From 9.0% to 26% nickel
From 1.0% to 8.0% copper
From 12% to 30% cobalt
From 5.5% to 10% aluminium
From approximately 4.0% to 7.0% titanium
From 0.4% to 2.0% silicon
Remainder substantially all iron

the sum of the nickel content plus 0.5 the cobalt content plus 0.5 the copper content lying between 24 and 36%, the silicon/aluminium ratio lying within the limits 1:20 and 1:4, the silicon/titanium ratio lying above 1:10, and the titanium/aluminium ratio lying below 1:1, and the aluminium, silicon and titanium contents being so adjusted to the nickel, cobalt and copper contents of the alloy that the following relation applies: aluminium plus 1.2 silicon content plus 0.4 titanium content plus or minus a maximum of 1.2=0.31 (nickel plus 0.5 cobalt content plus 0.5 copper content).

2. Permanent magnet made from an alloy consisting of:

From 20% to 26% nickel
From 1.0% to 8.0% copper
From 12% to 30% cobalt
From 5.5% to 10% aluminium
From approximately 4.0% to 7.0% titanium
From 0.4% to 2.0% silicon
Remainder substantially all iron

the sum of the nickel content plus 0.5 the cobalt content plus 0.5 the copper content lying between 24 and 36%, the silicon/aluminium ratio lying within the limits 1:20 and 1:4, the silicon/titanium ratio lying above 1:10, and the titanium/aluminium ratio lying below 1:1, and the aluminium, silicon and titanium contents being so adjusted to the nickel, cobalt and copper contents of the alloy that the following relation applies: aluminium plus 1.2 silicon content plus 0.4 titanium content plus or minus a maximum of 1.2=0.31 (nickel plus 0.5 cobalt content plus 0.5 copper content), the said nickel content promoting high coercivity with a relatively low cobalt content compared with the nickel content.

3. Permanent magnet made from an iron-nickel - aluminium - cobalt - copper - titanium-silicon alloy and consisting of:

From 9.0% to 26.0% nickel
From 1.0% to 8.0% copper
From 12.0% to 30% cobalt
From 5.5% to 10.0% aluminium
Approx. 4.0% up to 7.0% titanium
From 0.4% to 2.0% silicon
Remainder substantially all iron

the sum of the nickel content plus 0.5 the cobalt content plus 0.5 the copper content lying between 24 and 36%, the silicon/aluminium ratio lying within the limits 1:20, and 1:4, the silicon/titanium ratio lying above 1:10, and the titanium/aluminium ratio lying below 1:1, and the aluminium, silicon and titanium contents being so adjusted to the nickel, cobalt and copper contents of the alloy that the following relation applies: aluminium plus 1.2 silicon content plus 0.4 titanium content plus or minus a maximum of 0.5 equals 0.31 (nickel plus 0.5 cobalt plus 0.5 copper content).

4. Permanent magnet made from a substantially iron-nickel-aluminium-cobalt-copper alloy with silicon and consisting of:

From 20.0% to 26% nickel
From 1.0% to 8% copper
From 12.0% to less than the chosen nickel content of cobalt
From 5.5% to 10% aluminium
From 0.3% to 2% silicon
Remainder substantially all iron

the sum of the nickel content plus 0.5 the cobalt content plus 0.5 the copper content lying between 24 and 36%, the silicon/aluminium ratio lying within the limits 1:20 and 1:4 and the aluminium and silicon contents being so adjusted to the nickel, cobalt and copper contents that the following relation applies: aluminium plus 1.2 silicon content plus or minus a maximum of 1.2 equals 0.31 (nickel plus 0.5 cobalt content plus 0.5 copper content), the cobalt content being low relatively to the nickel content.

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