

PATENT SPECIFICATION

(11) 1 544 601

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- (21) Application No. 6012/77 (22) Filed 14 Feb. 1977
 (31) Convention Application No. 51/015195
 (32) Filed 14 Feb. 1976 in
 (33) Japan (JP)
 (44) Complete Specification published 19 April 1979
 (51) INT CL² C22C 38/30 19/07 27/06
 (52) Index at acceptance



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C7A 716 744 745 746 748 770 782 783 784 A231 A233 A235
 A237 A239 A23Y A241 A24X A250 A253 A255 A257
 A259 A25Y A260 A28X A28Y A30Y A329 A339 A33Y
 A349 A34Y A35Y A369 A37Y A389 A390 A394 A396
 A398 A39Y A400 A402 A404 A406 A40Y A41Y A439
 A459 A48Y A509 A529 A549 A55Y A579 A599 A609
 A61Y A629 A671 A673 A675 A677 A679 A67X A681
 A683 A685 A687 A689 A68X A693 A695 A697 A699
 A69X A70X

(54) IMPROVEMENTS RELATING TO MAGNETIC MATERIALS

(71) We, INOUE - JAPAX RESEARCH INCORPORATED of 5289 Aza Michimasa, Nagatsudamachi, Midoriku, Yokohamashi, Kanagawaken, Japan, a Japanese company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an Iron/Chromium/Cobalt-Base Sponodal Decomposition-Type Magnetic Alloy or alloy system and, more particularly, to an improved composition of such an alloy system which makes possible the preparation of a magnetic alloy body in a simplified procedure while exhibiting a magnetic performance comparable with or even better than, those of the alloys of this type heretofore proposed. Thus the invention also includes within its scope a permanent magnetic body comprising such an alloy and a method of making a permanent magnet from such an alloy.

As pointed out in British Patent Specification No. 1,367,174, published September 18 1974, the iron/chromium alloy system has, in its composition diagram, a "limit of metastability" or "spinodel" which is thermodynamically defined as the locus of disappearance of the second derivative of the Helmholtz free energy with respect to the composition of the system. When a high-temperature composition, which is of homogeneous single phase structure (α -phase), of the alloy is brought within the spinodel in a lower temperature range, it is transformed into a separated two-phase structure ($\alpha_1 + \alpha_2$), the phase separation being called "spinodal decomposition". The

decomposed alloy has a periodic microstructure generally in the order of hundreds of angstroms and which consists of two composition modulated isomorphous phases in which one phase (α_1) is in the form of a fine precipitate uniformly distributed in another phase (α_2) which forms the matrix. It is observed if the first phase in such a microstructure is magnetic, and the second is nonmagnetic, there results a single-domain structure whereby a highly retentive magnetic body can be obtained.

Said British patent discloses that the iron/chromium alloy of spinodal decomposition-type, when it contains cobalt, optionally also with one or both of molybdenum and tungsten in the proportions set forth therein, represents an improved magnetic-material system whose magnetic retentivity and magnetic energy product are comparable with or generally even higher than, those of "Alnico" (iron/aluminium/nickel/cobalt) alloys which have hitherto been the mainstay in the magnetic industry. In addition to their excellent magnetic properties, the improved alloys have, because of their constituent metals, the advantages of lower material cost and better workabilities than conventional alloys. It has also been taught that addition of silicon up to a certain proportion moderates the heat-treatment conditions required to accomplish the spinodal decomposition of the alloys without materially decreasing the desirable magnetic properties attainable therewith. The art has also recognized that addition of one or more of the incidental ingredients manganese, nickel, titanium, copper, aluminium, niobium and tantalum in a small proportion may be advantageous as is

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the addition of those incidental ingredients mentioned above.

As noted above, the desirable magnetic characteristics of the alloy are imparted when the high-temperature homogeneous single phase, i.e. the α -phase, decomposes into the two isomorphous phases, i.e. the α_1 and α_2 phases, past the spinode. Accordingly, the method of preparing a magnetic body of the improved alloy system comprises the procedures required to effect the spinodal decomposition of the alloy of a preselected composition. The composition may be prepared by melting constituent metals or components together in a suitable furnace or crucible and then casting the melt to form ingots. While such ingots may, after machining to a suitable dimension, be subjected directly to the treatment procedures, it is possible to convert the alloyed ingot into a powder and then to compact and sinter the particles to a coherent body of a desired geometry. In order to effect the spinodal decomposition, while a gradual cooling may be employed to transform the alloy from the high-temperature phase to the isomorphous phases, the following steps have been found more practical and highly suitable. The initial step comprises solution-treatment which includes heating at an elevated temperature for a substantial period of time and subsequent quenching to bring the homogenized high-temperature α -phase to room temperature. The quenched body is then tempered or aged whereby the spinodal decomposition to α_1 and α_2 phases is obtained. The solution-treatment may be preceded by hot or cold working. The tempering is preferably done stepwise at different temperatures. The solution-treated body is preferably subjected to an isothermal treatment in a magnetic field prior to the final tempering treatment. Magnetic properties of the body are generally improved when a cold working step is incorporated prior to a final quenching step and subsequent to a preliminary tempering step or the magnetic treatment step.

With the previously used compositions, however, to accomplish the solution-treatment successfully and thus to form the homogeneous single phase α and bring the same to room temperature or to the ageing temperature requires heating to as high as 1300°C and subsequent quenching at a cooling rate as high as 200°C/sec. Heating to such a high temperature is also required when hot working of the alloy ingot is to be done prior to the solution-treatment. While, as taught in said British patent, the quenching rate can be lowered substantially by having the alloy contain silicon in the range as specified, the high-temperature

heating requirements have imposed great difficulties on the manufacturing process and left much to be desired in the economy of the magnets produced.

In order to overcome these difficulties, efforts have been made to explore a further component or components effective to extend the domain of the homogeneous α phase of the alloy system thereby enabling the alloy to be solution-treated and hot worked at a lower, more practical temperature than the conventional composition while retaining excellent magnetic properties and an improved cold workability. Thus, for example, in British Patent Specification No. 1,435,684, published September 8 1976, the inventor has already disclosed an improved spinodal decomposition-type alloy of the class described which by weight consists of 3 to 20% cobalt, 10 to 40% chromium, 0.2 to 5% of one or both of niobium and tantalum, 0 to 5% aluminium and the balance iron. As taught therein the addition of one or both of niobium and tantalum preferably also with 0.2 to 5% aluminium is effective to extend the domain of the α phase while reducing the γ phase of the alloy system, thus making it possible to accomplish the solution-treatment at a temperature as low as 900°C or even about 650°C, depending upon the relative alloy compositions.

The above proposed alloy, however, still has drawbacks arising from the fact that, to be effective or for better results, it commonly requires the addition of aluminium besides niobium and/or tantalum. A melt of the alloy with added aluminium gives rise to handling difficulties in casting and tends to yield irregular products. Moreover, while the use of the best process parameters and composition has allowed the alloy to achieve a maximum energy product as high as 5.7×10^6 G · Oe (with cold working) and 4.7×10^6 G · Oe (without cold working), the magnetic performance typically attainable by procedures currently adoptable for mass production is limited to 4×10^6 G · Oe or less and cannot be said to be satisfactory.

It is, therefore, the principal object of the present invention to provide a still improved composition for an iron/chromium/cobalt-base spinodal decomposition-type magnetic alloy whereby the afore-mentioned problems associated with the compositions proposed heretofore are substantially reduced or eliminated. A specific object of the invention is to provide an improved alloy of the class described and containing a novel component which is effective in extending the domain of the homogeneous α phase of the alloy system thereby enabling the alloy to be solution-treated and hot worked at a

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much decreased temperature or to the extent that the solution-treatment can be effected at a desired temperature or that such step can even be dispensed with while achieving excellent magnetic properties and retaining an improved cold workability.

We have found that addition of vanadium is effective to extend the domain of the α phase while diminishing the domain of the γ phase, of the iron/chromium/cobalt-base alloy system, to improve the magnetic properties and yet to retain a melt of the alloy under satisfactory conditions for casting.

According to the invention, in a first aspect thereof, a spinodal decomposition-type magnetic alloy which comprises by weight 3 to 30% cobalt, 10 to 40% chromium and 0.1 to 15% vanadium, and the balance being iron and incidental ingredients and impurities well known in the art;

In accordance with a second aspect of the invention, there is provided a method of making a permanent magnet which comprises the steps of: forming a body of a spinodal decomposition-type magnetic alloy of the following composition: 3 to 30% by weight cobalt, 10 to 40% by weight chromium, 0.1 to 15% by weight vanadium and the balance being iron and incidental ingredients and impurities well known in the art; casting the admixture of these ingredients to form said body; solution heat treating said body followed by quenching thereof; tempering the body in a magnetic field; and step-tempering said body at successively decreased temperatures.

The above and other objects, features and advantages of the invention will become more readily apparent from the following exemplary description, reference being made to the accompanying drawings, in which:

Fig. 1 is a cross-sectional phase diagram of a vanadium-containing iron/chromium/cobalt alloy and vanadium proportions being fixed by weight at 15% and 5%, respectively.

Figs. 2 and 3 are graphs showing, respectively the maximum energy product $(B \cdot H)_m$ and the residual flux density B_r plus the coercive force H_c of the exemplary alloy composition of Fig. 1;

Figs. 4 and 5 are characteristic phase diagrams obtained with vanadium and cobalt proportions of the alloy in the cross-sectional phase diagram of Fig. 1 varies with respect to fixed cobalt and vanadium proportions respectively.

Referring now to Fig. 1 which illustrates the cross-sectional phase diagram of an Fe-Cr-15% Co-5% V alloy composition, a large domain of the homogeneous α

phase exists. Thus, when, for example, the composition containing 23% by weight chromium (23% Cr-15% Co-5% V-57% Fe) is taken, it is seen that the single domain α phase extends from the high-temperature range to 600°C. This indicates that the solution-treatment can be carried out substantially at any temperature higher than 600°C (practically at any temperature higher than 700°C to 800°C, that is slightly above the spinodal decomposition temperature). With the composition containing 20% by weight Cr chosen, the diagram shows that there is solely in existence the single domain α phase extending from the high-temperature to low-temperature ranges, indicating that the cast alloy body does not require the solution-treatment and, without undergoing it, can be directly brought to a subsequent production step required to produce the hard or semihard magnetic characteristics desired.

It is further noted that if the chromium content is increased up to 28%, a heating temperature of about 1000°C suffices. Although not shown, it has been found that if it is increased to 40%, a temperature of about 1100°C is sufficient for the solution treatment.

It should be noted at this point that when the chromium content in the iron-chromium-cobalt alloy here concerned is increased above 40%, the proportion of the non-magnetic phase markedly increases resulting in a reduction of magnetic performance to an unacceptable extent due to the decrease of residual flux density B_r as shown in Fig. 3 and also the alloy becomes excessively hard and brittle. For this reason, it is necessary to define the upper limit of chromium amount at 40% and, preferably 35% by weight.

This is apparent also from Fig. 4 showing that the increase of the solution-treatment temperature required due to a higher chromium content can be controlled by increasing the content of vanadium for a given cobalt content and from Fig. 5 showing that such increase of the solution-treatment temperature can also be controlled by decreasing the content of cobalt for a given vanadium content.

Figs. 2 and 3 show that when the alloy has the chromium content reduced around to 19%, its maximum energy product $(B \cdot H)_m$ drops sharply as does its coercive force (H_c). By increasing the content of cobalt, the range of chromium content in which good magnetic properties are obtained may extend down to around 15%. The lower limit of chromium content is thus defined at 10% and preferably 15% by weight, at which the proportion of the non-magnetic phase necessary to impart the desired

coercive force to the alloy becomes insufficient and the solution-treatment also becomes difficult.

5 The alloy hardly undergoes the spinodal decomposition and its attainable coercive force is sharply reduced when the cobalt content is less than 3%. Accordingly, the lower limit of cobalt is defined at 3% and preferably 5%. As noted from Fig. 5, the temperature required for solution-treatment rises as the cobalt content is increased even with a decreased chromium content and with the vanadium additive incorporated. Since the attainment of the solution-temperature thus becomes difficult and the plastic workability also deteriorates when the cobalt content reaches 30%, its upper limit is defined at 30% and preferably 25% by weight.

10 As noted previously, the addition of vanadium is effective to enlarge the single α -phase domain of the ternary *Fe-Cr-Co* alloy to an extent which has not been possible heretofore. Specifically, it is capable of bringing the lower *Cr* boundary of the single phase domain down to 15%. For comparison, reference is made to the earlier development of *Fe-Cr-Co-Nb-Al* noted hereinbefore in which the lowest *Cr* boundary which was possible was 23%. Thus, the *V* additive makes the solution-treatment unnecessary over an extended range of the base alloy composition and, as a consequence, facilitates the heat treatment and also, if to be conducted, the hot working. It also facilitates the casting procedure and the alloy has an excellent cold workability.

15 The effective amount of vanadium to be incorporated into the base *Fe-Cr-Co* alloy in accordance with the invention lies between 0.1 and 15% by weight, its lower limit being preferably 0.5% by weight.

20 Thus, the improved magnetic alloy according to the invention has the following preferred composition 5 to 25% by weight *Co*, 15 to 35% by weight *Cr*, 0.5 to 10% by weight vanadium and the balance iron.

EXAMPLE

25 An alloy containing by weight 15% cobalt, 22% chromium, 5% vanadium and balance iron was prepared by melting an admixture of these ingredients in a high-frequency induction furnace in an argon atmosphere to form a cast body or ingot thereof. The ingot was hot or cold worked into a diameter of 10 mm. The solution-treatment was carried out by heating the worked body at a temperature of 900°C for 1 hour and then water-quenching it to room temperature. Although 700°C may be sufficient for solution-treatment as is apparent from Fig. 1, the temperature of 900°C was employed in consideration of

the treatment time. The ingot was next tempered at 640°C in a magnetic field of 4000 Oersted for 1 hour and then at 580°C for 1 hour, then at 560°C for 1 hour and finally at 540°C for 5 hours this is known as step-tempering. The resultant body has a residual flux density *Br* of 12700 Gauss, a coercive force *Hc* of 580 Oersted and a maximum energy product (*B · H*)_m of 4.4×10^6 Gauss · Oersted.

When the content of chromium in the above alloy was varied, the phase diagram shown in Fig. 1 was obtained and the residual flux density, the coercive force and the maximum energy product varied as shown in Figs. 2 and 3.

Also, when the content of cobalt and the content of vanadium were each varied, the characteristic diagrams shown in Figs. 4 and 5 were obtained and the values of the residual flux density, coercive force and maximum energy product as shown in Figs. 2 and 3 were each found to drop by an amount of between 0 and 20%. From this, the composition 15% *Co*-22% *Cr*-5% *V*-58% *Fe*, as used in this Example, appears to be the optimum composition, exhibiting most excellent magnetic properties.

When, in the above process, a cold working step was introduced between the magnetic tempering and the step-tempering stages, the magnetic properties of the alloy were found to be enhanced markedly. Thus, a maximum energy product (*B · H*)_m of 6.2×10^6 Gauss · Oersted was obtained when a reduction of 50 to 60% was employed. The values of maximum energy product obtained varied with variation of chromium content with the use of this cold working and are plotted along the broken line in the diagram of Fig. 2.

The strength of the magnetic field, the temperature and the heating time in the magnetic tempering stage described above may be varied from 2000 to 4000 Oersted, from 600 to 680°C and from 10 minutes to 2 hours, respectively. The addition of vanadium was also found to permit the temperatures of the final step of the step-tempering to be reduced to 400°C.

It should be understood that the improved alloy in accordance with the invention as described in the foregoing does not exclude the addition of incidental ingredients which together with their respective ranges of proportions, are well known in the art.

WHAT WE CLAIM IS:—

1. A spinodal decomposition-type magnetic alloy which comprises by weight 3 to 30% cobalt, 10 to 40% chromium and 0.1 to 15% vanadium and the balance being iron and incidental ingredients and impurities well known in the art.



coercive force to the alloy becomes insufficient and the solution-treatment also becomes difficult.

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2. The alloy defined in Claim 1 which contains 0.5 to 10% by weight vanadium.
3. The alloy defined in Claim 1 or Claim 2 which contains 5 to 25% by weight cobalt.
- 5 4. The alloy defined in any of the preceding claims which contains 15 to 35% by weight chromium.
- 10 5. A magnetic composition which comprises an alloy according to Claim 1 substantially as hereinbefore described with reference to any one of the accompanying drawings.
- 15 6. A magnetic composition which comprises an alloy according to Claim 1 substantially as hereinbefore described with reference to the Example.
- 20 7. A permanent magnetic body comprising an alloy of any one of the preceding claims when magnetised.
- 25 8. A method of making a permanent magnet which comprises the steps of: forming a body of a spinodal decomposition-type magnetic alloy of the following composition: 3 to 30% by weight cobalt, 10 to 40% by weight chromium, 0.1 to 15% by weight vanadium and the balance being iron and incidental ingredients and impurities well known in the art; casting the admixture of these ingredients to form said body; solution heat treating said body followed by quenching thereof; tempering the body in a magnetic field; and step-tempering said body at successively decreased temperatures.
- 30 9. A method according to Claim 8 in which said alloy contains 5 to 25% by weight cobalt, 15 to 35% by weight chromium, 0.5 to 10% by weight vanadium and the balance iron.
- 35 10. A method according to Claim 8 or Claim 9 further comprising the step of cold working said body subsequent to the magnetic tempering and prior to the step-tempering thereof.
- 40 11. A permanent magnet when made by a method according to any one of Claims 8 to 10.
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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1979
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.