

SPECIFICATION

Fe-Cr-Co permanent magnet alloy

- 5 The invention is concerned with Fe-Cr-Co magnetic materials. 5
- Magnetic materials suitable for use in relays, ringers, and electro-acoustic transducers such as loudspeakers and telephone receivers characteristically exhibit high values of magnetic coercivity, remanence, and energy product.
- Among established alloys having suitable magnetic properties are Al-Ni-Co-Fe and Cu-Ni-Fe 10 alloys which are members of a group of alloys considered to undergo spinodal decomposition resulting in a fine-scale two-phase microstructure. Recently, alloys containing Fe, Cr and Co have been investigated with regard to potential suitability in the manufacture of permanent magnets. Specifically, certain ternary Fe-Cr-Co alloys are disclosed in H. Kaneko et al, "New Ductile Permanent Magnet of Fe-Cr-Co Systems", *AIP Conference Proceedings* No. 5, 1972, p. 15 1088, and in U.S. patent 3,806,336, "Magnetic Alloys". Quaternary alloys containing ferrite forming elements such as, e.g., Ti, Al, Si, Nb or Ta in addition to Fe, Cr and Co are disclosed in U.S. patent 3,954,519, "Iron-Chromium-Cobalt Spinodal Decomposition Type Magnetic Alloy Comprising Niobium and/or Tantalum", in U.S. patent 3,989,556, "Semihard Magnetic Alloy and a Process for the Production Thereof", in U.S. patent 3,982,972, "Semihard Magnetic 20 Alloy and a Process for the Production Thereof", and in U.S. patent 4,075,437, "Composition, Processing, and Devices Including Magnetic Alloy". 20
- The use of ferrite forming elements such as, e.g., Ti, Al, Si, Nb or Ta in quaternary alloys has been advocated, especially at higher Co levels or in the presence of impurities such as, e.g., C, N or O, to facilitate production of a preliminary fine-grained alpha phase structure by low- 25 temperature annealing. 25
- According to one aspect of the present invention there is provided a Fe-Cr-Co magnetic alloy consisting of 25-29 wt.% Cr, 7-12 wt.% Co, remainder Fe with or without impurities, said alloy having at least 3000 grains per mm³, a coercive force in the range of 300-600 Oersted, a remanence in the range of 8000-13000 Gauss, and a magnetic energy product in the range of 30 1-6 MGOe. 30
- The embodiment of the invention provides a ternary Fe-Cr-Co magnetic alloy whose grain size is sufficiently fine to result in at least 3000 grains per mm³ and which has a coercive force in the range of 300-600 Oersted, a remanence in the range of 8000-13000 Gauss, and a maximum magnetic energy product in the range of 1-6 MGOe. The alloy comprises 25-29 35 weight percent Cr, 7-12 weight percent Co, and remainder Fe with or without impurities, and may be conveniently produced, e.g., by a process involving solution annealing at a temperature in the range of 650-1100 degrees C to produce a fine-grained, essentially single phase alpha structure, followed by cold forming and aging. Magnets made from such alloys may be used e.g., in electro-acoustic transducers such as loudspeakers and telephone receivers, in relays, and 40 in ringers. 40
- For a better understanding of the invention, reference is made to the accompanying drawing, in which the single Figure shows phase diagrams of two Fe-Cr-Co alloy systems containing 9 weight percent Co and 11 weight percent Co, respectively.
- In accordance with the invention it has been realised that Fe-Cr-Co alloys containing Cr in a 45 preferred range of 25-29 weight percent, Co in a preferred range of 7-12 weight percent, and remainder Fe with or without impurities can be produced so as to simultaneously have a maximum energy product in the range of 1-6 MGOe and a grain size corresponding to at least 3000 grains per mm³, such grain structure being particularly beneficial when the alloy is to be cold shaped. A more narrow range of Cr content may be preferred and, specifically, in the 50 interest of optimising alloy formability, an upper limit of 28 weight percent and, in the interest of optimising magnetic properties, a lower limit of 26 weight percent Cr may be preferred. 50
- Alloys of the embodiment may be prepared, e.g. by casting from a melt of constituent elements Fe, Cr and Co or their alloys in a crucible or furnace such as, e.g., an induction furnace. Alternatively, a metallic body having a composition within the specified range may be 55 prepared by powder metallurgy. Preparation of an alloy and, in particular, preparation by casting from a melt calls for care to guard against inclusion of excessive amounts of impurities as may originate from raw materials, from the furnace, or from the atmosphere above the melt. If such care is taken and, in particular, if sufficient care is taken to minimise the presence of impurities such as, e.g., nitrogen, addition of ferrite forming elements may be dispensed with. To minimise 60 oxidation or excessive inclusion of nitrogen, it is desirable to prepare a melt with slag protection, in a vacuum, or in an inert atmosphere such as, e.g., an argon atmosphere. Levels of specific impurities are preferably kept below 0.05 weight per cent C, 0.05 weight per cent N, 0.2 weight percent Si, 0.5 weight per cent Mg, 0.1 weight per cent Ti, 0.5 weight per cent Ca, 0.1 weight per cent Al, 0.5 weight percent Mn, 0.05 weight percent S, and 0.05 weight percent O. 60
- 65 Typical processing of the alloy after casting is as follows. The alloy is soaked at a temperature 65

at which the alloy is in a two-phase, alpha plus gamma state for a period of 1–10 hours, temperatures in the range of 1100–1300 degrees C being generally appropriate for this purpose. More specific preferred limits on such temperature corresponding to alloys containing, respectively, 9 weight percent Co and 11 weight percent Co can be obtained from the Figure.

5 The alloy is then hot worked in such two-phase state, e.g., by hot rolling, forging, or extruding to break down the as-cast structure and, if desired, the alloy may be shaped by cold working. In order to develop a uniformly fine grain structure, the alloy is then solution annealed at a temperature at which the alloy is in an essentially single-phase alpha state and which preferably is in the range of 650–1100 degrees C. Preferred upper limits on annealing temperature for
10 specific alloys may be conveniently obtained by approximate linear interpolation between the following values: 950 degrees C for an alloy containing 25 weight percent Cr and 7 weight percent Co, 875 degrees C for an alloy containing 25 weight percent Cr and 12 weight percent Co, 1100 degrees C for an alloy containing 29 weight percent Cr, and 7 weight percent Co, and 975 degrees C for an alloy containing 29 weight percent Cr and 12 weight percent Co and
15 are preferred not to exceed 1000 degrees C in the interest of minimisation of grain growth. In the interest of improved kinetics, a lower limit of 800 degrees C is further preferred and, in the interest of minimising gamma phase, preferred upper limits are obtained by approximate linear interpolation between respective values of 925 degrees C, 850 degrees C, 1075 degrees C, and 950 degrees C.

20 If the alloy has been cold worked, solution annealing so as to substantially recrystallise and homogenise the alloy may take from 10 minutes to 2 hours depending on annealing temperature and size of ingot. More typically, time required is in the range of 30–90 minutes. Solution annealing may be performed in air or, in the interest of minimising surface oxidation, under exclusion of oxygen.

25 Solution annealing is terminated by rapid quenching, e.g., by water or brine quenching, or, in the case of thin strips, by air quenching and preferably so as to result in a cooling rate of at least 1000 degrees C/min. throughout the alloy. At this point, the alloy is at or near room temperature, i.e., at a temperature which does not exceed 100 degrees C, and has an essentially uniformly fine grain size not exceeding 70 micrometers (corresponding to at least
30 3000 grains per mm³). Such grain structure is much finer than the coarse structure obtained by annealing at elevated temperature.

A comparison of the grain structure of an alloy containing 28 weight percent Cr, 11 weight percent Co, remainder iron annealed at 900 degrees C with the grain structure of the same alloy annealed at 1300 degrees C has revealed that the grain of the latter is very much coarser.

35 At a temperature not exceeding 100 degrees C, the alloy may then be cold formed, e.g., by bending, wire drawing, deep drawing, or swaging. Particular benefits are derived from the fine-grained structure if the alloy is to cold formed by wire drawing, deep drawing, or bending, i.e., by a technique which causes at least local tensile deformation. On account of the uniformly fine grain structure of the alloy as annealed and quenched, drawing may be by an amount
40 corresponding to an essentially cross-sectional area reduction of at least 50 percent. Similarly, bending may result in a change of direction of at least 30 degrees, the resulting radius of curvature being such that it does not exceed a value which is proportional to the change in direction, which for a 30 degree change of direction is equal to the thickness of the part being bent, and which for a 90 degree change of direction is equal to 4 times the thickness of the part
45 being bent.

Processing as described above characteristically comprises a step of maintaining the alloy at a temperature or within a temperature range corresponding to an essentially single phase alpha state. Alternate processing so characterised may be, e.g., by hot working with finishing temperature in an essentially single phase alpha range, cooling, and forming. Moreover, forming
50 may be carried out in stages with intermediate additional solution annealing and quenching. Additional processing steps such as e.g., machining by drilling, turning, or milling before or after forming are not precluded.

The shaped alloy is finally subjected to an aging treatment to develop magnetic hardening. Such aging treatment may follow any of a variety of schedules, for example as disclosed in U.S.
55 patent No. 4,075,437 which allow the production of magnets having magnetic remanence of 8000–13000 Gauss, magnetic coercivity of 300–600 Oersted, and magnetic energy product of 1–6 million Gauss-Oersted. Accordingly, such alloys may serve, upon magnetisation in a magnetic field, as magnets in relays, ringers, and electro-acoustic transducers such as loud-speakers and telephone receivers.

60 In the following examples, phase structure and grain size were determined by X-ray diffraction analysis, hardness measurements, and metallographic analysis of microstructure after solution annealing and quenching, but before cold shaping. Average grain size was in the range of 25–40 micrometers as shown in Table I. Also shown in Table I are magnetic remanence B_r, coercivity H_c, and energy product (BH)_{max} determined after aging of the alloys.

Example 1

An ingot of an alloy containing 26.8 weight percent Cr, 9.4 weight percent Co, and balance Fe with or without impurities was cast from a melt. Ingot dimensions were a thickness of 1.25 inches (31.8 mm.), a width of 5 inches (127 mm.), and a length of 12 inches (304.8 mm.).

- 5 The cast ingot was heated to a temperature of 1250 degrees C, hot rolled into a quarter inch (6.4 mm.) plate, and water cooled. Sections of the plate were cold rolled at room temperature into strips having a thickness of 0.1 inches (2.5 mm.) and a width of 0.625 inches (15.9 mm.). The strips were annealed at 900 degrees C for 30 minutes and water cooled. The strips were reheated to 630 degrees C, maintained at this temperature for 1 hour, cooled at an essentially
10 constant rate of 15 degrees C/h to a temperature of 555 degrees C, maintained at 540 degrees C for 3 hours, and maintained at 525 degrees C for 4 hours. 10

Example 2

- 15 Strips of an alloy containing 27.7 weight percent Cr, 10.9 weight percent Co, and balance Fe with or without impurities were prepared by casting, hot working, quenching, solution annealing, cooling and rolling as described in Example 1. The strips were reheated to 635 degrees C, maintained at this temperature for 3 minutes, cooled at an essentially constant rate of 15 degrees C/h to 555 degrees C, maintained at 540 degrees C for 5 hours and maintained at 525 degrees C for 4 hours. 15

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Example 3

- Strips of an alloy containing 27.3 weight percent Cr, 7.2 weight percent Co, and balance Fe with or without impurities were prepared as described in Example 1. The strips were reheated to 620 degrees C, maintained at this temperature for 1 hours, cooled at an essentially constant
25 rate of 15 degrees C/h to 555 degrees C, maintained at 555 degrees C for 2 hours, at 540 degrees C for 3 hours, and at 525 degrees C for 16 hours. 25

Example 4

- 30 Strips of an alloy containing 26.8 weight percent Cr, 10.6 weight percent Co, and balance Fe with or without impurities were prepared as described in Example 1. The strips were soft and ductile and could readily be bent in any direction by 90 degrees over a sharp edge having a radius of curvature of 1/32 of an inch (0.08 mm.) or drawn so as to result in 99 percent area reduction. Strips were aged by maintaining the alloy at a temperature of 680 degrees C for 30 minutes, rapidly cooling at a first rate of 140 degrees C/h to 615 degrees C, and then cooling
35 at exponentially decreasing rates of from 20 to 2 degrees C/h to a temperature of from 525 degrees C. 35

Example 5

- 40 0.7 inch (17.8 mm.) diameter rods of an alloy containing 27.9 weight percent Cr, 10.7 weight percent Co, and balance Fe were prepared by casting, hot working, solution annealing, and quenching. The rods were cold drawn to 0.07 inch (1.78 mm.) diameter wire (having 99 percent reduced cross-sectional area), solution annealed at 930 degrees C for 30 minutes, and cooled to room temperature. An aging heat treatment was carried out by maintaining the drawn wire for 30 minutes at 700 degrees C, cooling to 615 degrees C at a rate of 30 degrees C/h in
45 a magnetic field of 1000 Oersted, and cooling to a temperature of 480 degrees C at exponentially decreasing rates of from 20 to 2 degrees C/h. 45

TABLE I

Ex.	Cr Wt. %	Co Wt. %	Grain Size μm	B_r G	H_c Oe	$(BH)_{\text{max}}$ MGOe
1	26.8	9.4	30	10010	380	1.55
2	27.7	10.9	25	9750	400	1.72
3	27.3	7.2	40	9280	300	1.10
4	26.8	10.6	40	10010	370	1.76
5	27.9	10.7	30	12750	570	5.03

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CLAIMS

1. A Fe-Cr-Co magnetic alloy consisting of 25-29 wt.% Cr, 7-12 wt.% Co, remainder Fe with or without impurities, said alloy having at least 3000 grains per mm^3 , a coercive force in the range of 300-600 Oersted, a remanence in the range of 8000-13000 Gauss, and a
65 magnetic energy product in the range of 1-6 MGOe. 65



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An ingot of an alloy containing 26.8 weight percent Cr, 9.4 weight percent Co, and balance Fe with or without impurities was cast from a melt. Ingot dimensions were a thickness of 1.25 inches (31.8 mm.), a width of 5 inches (127 mm.), and a length of 12 inches (304.8 mm.).

- 5 The cast ingot was heated to a temperature of 1250 degrees C, hot rolled into a quarter inch (6.4) mm.) plate, and water cooled. Sections of the plate were cold rolled at room temperature into strips having a thickness of 0.1 inches (2.5 mm.) and a width of 0.625 inches (15.9 mm.). The strips were annealed at 900 degrees C for 30 minutes and water cooled. The strips were reheated to 630 degrees C, maintained at this temperature for 1 hour, cooled at an essentially constant rate of 15 degrees C/h to a temperature of 555 degrees C, maintained at 540 degrees C for 3 hours, and maintained at 525 degrees C for 4 hours. 10 10

Example 2

Strips of an alloy containing 27.7 weight percent Cr, 10.9 weight percent Co, and balance Fe with or without impurities were prepared by casting, hot working, quenching, solution annealing, cooling and rolling as described in Example 1. The strips were reheated to 635 degrees C, maintained at this temperature for 3 minutes, cooled at an essentially constant rate of 15 degrees C/h to 555 degrees C, maintained at 540 degrees C for 5 hours and maintained at 525 degrees C for 4 hours.

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Example 3

Strips of an alloy containing 27.3 weight percent Cr, 7.2 weight percent Co, and balance Fe with or without impurities were prepared as described in Example 1. The strips were reheated to 620 degrees C, maintained at this temperature for 1 hours, cooled at an essentially constant rate of 15 degrees C/h to 555 degrees C, maintained at 555 degrees C for 2 hours, at 540 degrees C for 3 hours, and at 525 degrees C for 16 hours.

- 25 25

Example 4

Strips of an alloy containing 26.8 weight percent Cr, 10.6 weight percent Co, and balance Fe with or without impurities were prepared as described in Example 1. The strips were soft and ductile and could readily be bent in any direction by 90 degrees over a sharp edge having a radius of curvature of 1/32 of an inch (0.08 mm.) or drawn so as to result in 99 percent area reduction. Strips were aged by maintaining the alloy at a temperature of 680 degrees C for 30 minutes, rapidly cooling at a first rate of 140 degrees C/h to 615 degrees C, and then cooling at exponentially decreasing rates of from 20 to 2 degrees C/h to a temperature of from 525 degrees C.

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Example 5

0.7 inch (17.8 mm.) diameter rods of an alloy containing 27.9 weight percent Cr, 10.7 weight percent Co, and balance Fe were prepared by casting, hot working, solution annealing, and quenching. The rods were cold drawn to 0.07 inch (1.78 mm.) diameter wire (having 99 percent reduced cross-sectional area), solution annealed at 930 degrees C for 30 minutes, and cooled to room temperature. An aging heat treatment was carried out by maintaining the drawn wire for 30 minutes at 700 degrees C, cooling to 615 degrees C at a rate of 30 degrees C/h in a magnetic field of 1000 Oersted, and cooling to a temperature of 480 degrees C at exponentially decreasing rates of from 20 to 2 degrees C/h.

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TABLE I

50	Ex.	Cr	Co	Grain	B _r	H _c	(BH) _{max}	50
		Wt. %	Wt. %	Size μm	G	Oe	MGOe	
55	1	26.8	9.4	30	10010	380	1.55	55
	2	27.7	10.9	25	9750	400	1.72	
	3	27.3	7.2	40	9280	300	1.10	
	4	26.8	10.6	40	10010	370	1.76	
	5	27.9	10.7	30	12750	570	5.03	

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CLAIMS

1. A Fe-Cr-Co magnetic alloy consisting of 25-29 wt.% Cr, 7-12 wt.% Co, remainder Fe with or without impurities, said alloy having at least 3000 grains per mm³, a coercive force in the range of 300-600 Oersted, a remanence in the range of 8000-13000 Gauss, and a magnetic energy product in the range of 1-6 MGOe.

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2. An alloy according to claim 1, wherein the impurities are restricted to less than any of the following values 0.05 wt.% C, 0.05 wt.% N, 0.2 wt.% Si, 0.5 Wt.% Mg, 0.1 wt.% Ti, 0.5 wt.% Ca, 0.1 wt.% Al, 0.5 wt.% Mn, 0.05 wt.% S, and 0.05 wt.% O.

3. A method of producing an alloy according to claim 1 or 2, wherein the grain size is achieved by annealing heat treatment which is in the range of (a) 650–950°C when the alloy contains 25 wt.% Cr and 7 wt.% Co, (b) 650–875°C when the alloy contains 25 wt.% Cr and 12 wt.% Co, (c) 650–1100°C when the alloy contains 29 wt.% Cr and 7 wt.% Co, (d) 650–975°C when the alloy contains 29 wt.% Cr and 12 wt.% Co, and (e) in a range whose limits are obtained by substantial linear interpolation at intermediate levels of Cr and Co, wherein the alloy is formed into a desired body shape at a temperature not exceeding 100°C, and wherein the alloy is aged.

4. Method according to claim 3, wherein the annealing temperature is preferably in the range of 800–925 degrees C, 800–850 degrees C, 800–1075 degrees C and 800–950 degrees C for respective (a), (b), (c) and (d) alloy compositions.

5. Method according to claim 3 or 4, wherein the subjection of the body to the annealing is effected by solution annealing or hot working terminating at said annealing temperature.

6. Method according to claim 3, 4 or 5, wherein prior to the annealing the alloy is soaked at a temperature in the range of 1100–1300 degrees C; or after said soaking, additionally hot working the alloy at a temperature in the range of 1100–1300 degrees C; or after the said hot working, additionally cold working the body.

7. Method according to claim 3, 4, 5 or 6, wherein said forming is carried out in stages with additional intermediate solution annealing and quenching.

8. Method according to any one of preceding claims 3 to 7, wherein the aging is conducted by cooling at a substantially constant rate or cooling at a first, rapid average rate followed by cooling at a second slower average rate.

9. Method according to any one of the preceding claims, wherein the aging is carried out in the presence of a magnetic field.

10. Method according to any one of preceding claims, wherein the body is additionally machined after the annealing and prior to the forming step, and/or after the forming step and prior to the aging.

11. Method of producing an alloy, substantially as hereinbefore described with reference to any one of Examples 1 to 5 or to the Figure of the accompanying drawing.

12. A magnetic alloy produced by the method according to any one of claims 3 to 11.

