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MAGNETIC ALLOYS
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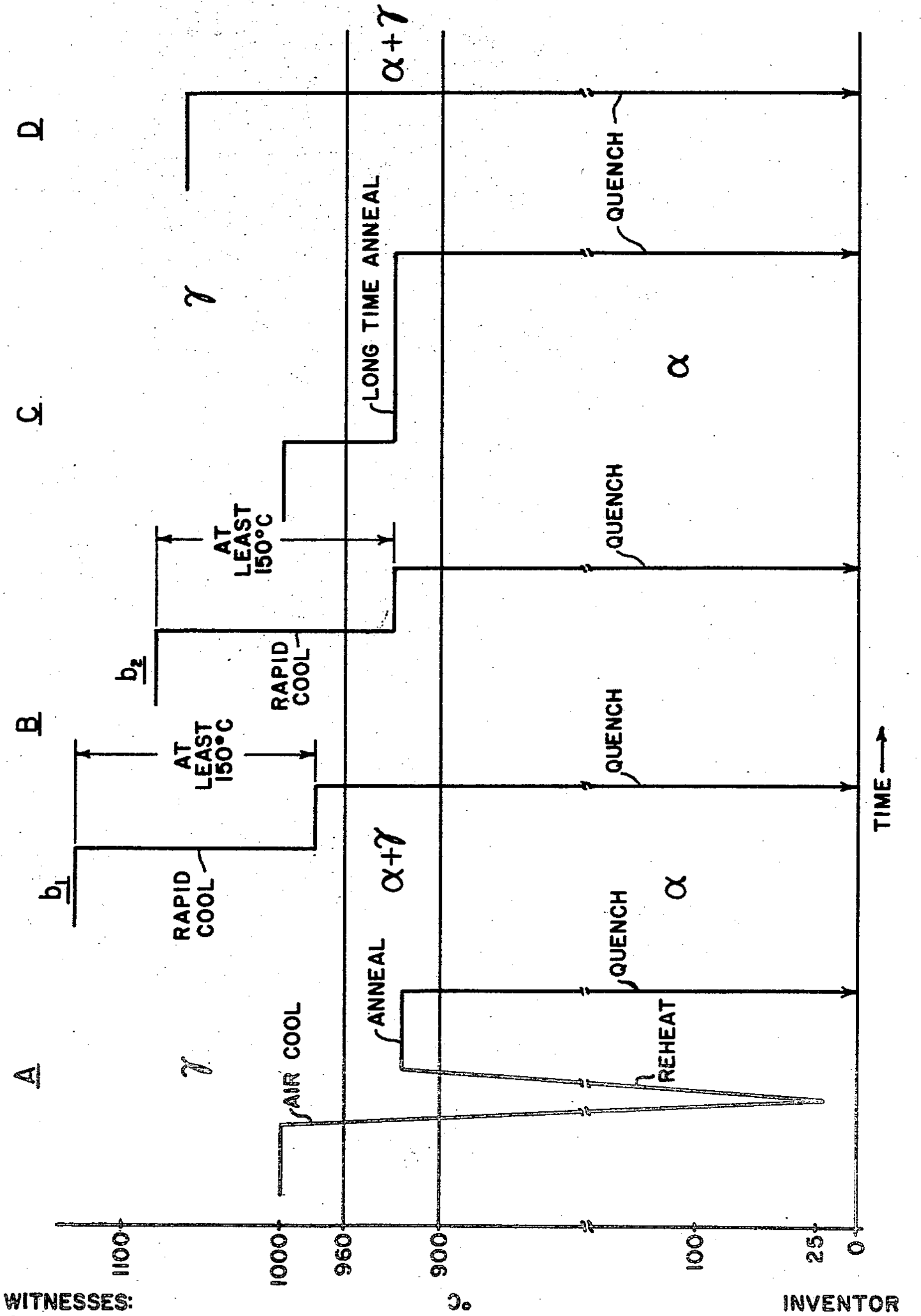

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PROCESSES FOR PRODUCING DUCTILE COBALT-IRON-VANADIUM MAGNETIC ALLOYS

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This invention is directed to processes capable of consistently producing cobalt-iron-vanadium alloys having good ductility for cold working into sheet form.

Cobalt-iron alloy magnetic material wherein cobalt and iron are in substantially equal amounts with or without small amounts of additives such as vanadium, has outstanding properties which make the alloys attractive for many applications and particularly for aircraft and military uses. These desirable properties are: (1) a high saturation induction, which makes possible drastic reductions in the size and weight of magnetic cores, (2) rectangular hysteresis loops when the alloy is suitably processed and annealed, which make the alloys applicable in saturable core devices, and (3) high Curie temperatures, which make them useful in elevated temperature environments.

The superior magnetic properties of cobalt-iron-vanadium alloys, particularly after a magnetic annealing treatment, has been known for some time. However, in spite of the great promise of the alloys, actual applications have been restricted to a very limited field. This has been due in large measure to the fact that with the processes which are currently available there has been an inability to consistently obtain a ductile product which may be cold worked into thin sheets.

Accordingly, it is a primary object of this invention to provide for a cobalt-iron-vanadium alloy a working and annealing schedule employing a final annealing in the alpha and gamma two-phase region prior to a final quench whereby a product having good ductility is obtained.

It is a further object of the invention to provide ductile, fine grained hot rolled sheets of cobalt-iron-vanadium alloys which can be readily cold rolled, by a process involving initially annealing the hot rolled sheets in the gamma range, cooling, annealing the sheets at a lower temperature in either the gamma region or the alpha-gamma region, and finally quenching the sheets.

It is an object of this invention to produce a ductile structure in cobalt-iron-vanadium alloys by annealing the alloys above the two-phase region, cooling the alloy, annealing the alloy within the two-phase region, and quenching.

It is another object of this invention to provide a process for making ductile sheets of an alloy composed of cobalt-iron-vanadium by working the alloy above the two-phase region, cooling to room temperature, reheating to and annealing in the alpha and gamma two-phase region, and then quenching.

Another object of the invention is to provide a process for producing ductile cobalt-iron-vanadium alloys which comprises annealing the alloys at temperatures above the two-phase region, cooling the alloys to a predetermined elevated temperature above the lower limit of the two-phase region and maintaining the alloys at that temperature for a predetermined time and thereafter quenching the alloys.

It is a further object of this invention to provide a process for producing ductile cobalt-iron-vanadium alloys which comprises annealing the alloys at temperatures above the two-phase region, cooling the alloys to a predetermined temperature within the two-phase region and holding at that temperature for a length of time sufficient to establish substantially equilibrium conditions in the alloys and then quenching.

Still another object of the invention is to provide a process for producing ductile cobalt-iron-vanadium alloys which comprises annealing the alloys at temperatures above the two-phase region, and then rapidly quenching the alloys.

Other objects of the invention will, in part, be obvious, and will, in part, appear hereinafter.

For a better understanding of the nature and objects of the invention, reference should be had to the following detailed description and to the figure, in which, graphs A, B, C and D depict the various heat treating cycles according to this invention.

The figure is particularly directed to cobalt-iron-vanadium alloys containing about 2% vanadium, but is typical of this alloy system. Changes in vanadium content will merely shift the limits of the two-phase field in which α (body centered cubic) and γ (face centered cubic) coexist. Hot working is performed in the γ field.

This invention is particularly directed to processes capable of developing ductile cobalt-iron-vanadium magnetic alloys containing, by weight, from 0.5% to 4% vanadium, substantially equal amounts of iron and cobalt, and small amounts of incidental impurities, which may be readily cold rolled so that relatively thin alloy sheets may be produced. Thereafter the cold rolled sheets are subjected to a final heat treatment for producing optimum magnetic properties.

Hot-rolled sheets of the cobalt-iron-vanadium alloys may be readily produced from ingots of the alloys, preferably vacuum cast ingots, of a thickness of about 0.1 inch. These hot-rolled sheets are quite brittle at room temperature, and the usual prior art practice is to anneal the hot rolled sheets to 900° C. and quench in brine and ice to produce a face centered cubic structure (see White Patent 1,862,559).

According to the present invention, it has been discovered that the hot rolled sheets can be subjected to a specified heat treatment with a final quench that results in a fine-grained martensitic structure which is quite ductile and can be readily cold rolled. In all cases the specified heat treatment of this invention comprises initially annealing the hot rolled sheet in the gamma region for a period of time. The sheet is then cooled, either slowly or rapidly to drop the temperature at least 150° C. and then annealed for a period of time at a temperature lower than the initial anneal temperature, in either the gamma region adjacent to the two-phase region or in the two-phase region, and then quenched to room temperature. This results in the desired martensitic grain texture with good cold workability in the sheet.

The upper and lower limits of the two-phase region vary with the concentration of vanadium in these alloys. With 2% vanadium, 49% cobalt, 49% iron alloys, the two-phase region extends from about 900° C. to about 960° C. The region contracts as the amount of vanadium is decreased (at 1% vanadium the range is approximately 960 to 985° C.), and expands with increasing amounts of vanadium (at 3% vanadium the range is 750° C. to 880° C.).

While the invention is described in connection with cobalt-iron-vanadium alloys in which the amounts of cobalt and iron are approximately equal, the invention is equally applicable to alloys containing, by weight, from 0.5% to 4% vanadium, from 30% to 70% cobalt, and the balance iron except for small amounts of incidental impurities.

In a preferred process corresponding to Curve A of the drawing, the alloy ingot is hot worked to sheet at a temperature above the two-phase alpha plus gamma region, the sheet is thereafter air cooled through the two-phase region to substantially room temperature, thereafter the sheet is reheated to a temperature within the two-phase region and maintained at that temperature for a period of at least about 50 minutes to produce a two-phase structure, the sheet is then rapidly quenched in a liquid medium to a temperature below room temperature to obtain a fine grain structure having a high proportion of martensite therein, and then the hot worked sheet is cold worked to thin gauge sheet.

A detailed description of this process is as follows:

PROCESS A

The success of this preferred process (graph A of the figure) depends upon obtaining as a final product a fine grained structure having a high proportion of martensite therein. It has been found in these cobalt-iron-vanadium alloys that, in addition to the well known transformation of gamma phase to alpha phase and the ordering of the alpha phase, a martensitic transformation can occur. Rapid cooling hinders the gamma to alpha transformation and converts the gamma phase through a diffusionless process to a body centered cubic structure of the martensitic type.

The microstructural changes which occur in this process might be outlined as follows: During hot rolling at temperatures above the two-phase region the microstructure is substantially entirely of the gamma phase. Air cooling to room temperature results in transformation of the bulk of the material to alpha phase but with a certain amount of martensite contained therein. The formation of two phases from a single phase which thus occurs tends to produce a fine grain structure. Reheating this material into the two-phase region produces a situation in which some of the alpha phase will change into the gamma phase. Thus, in the two-phase region the gamma and alpha phases will coexist with martensite. Rapid quenching of this material to room temperature or below results in transformation of the gamma phase to martensite but does not affect the alpha phase and the martensite existing in the two-phase region. This rapid quenching thus preserves the structure of fine grain, closely spaced precipitates of which martensite forms a very substantial proportion. The structure thus formed has good ductility.

As an example of this first process of the invention, some data are given in the following Table I on heats which were air cooled from a temperature of 1000° C. to 25° C., then rapidly heated to a temperature in the range of from 900° C. to 960° C., maintained at temperature for from 100 to 10,000 minutes and then rapidly cooled from the elevated temperature to a temperature of about 0° C. The samples tested contain, by weight, about 2% vanadium, balance essentially equal amounts of iron and cobalt.

Table I

Sample No.	Heat treatment		Microstructure		True stress at fracture, p.s.i.×10^3	Elongation, percent	Reduction of area, percent	Fracture mode
			Matrix	High temp. precip.				
223	1,000° C, 1 hr.; air cool to 25° C.; rapid reheat to 900° C.; quench to ° C.	100 min. at 900° C	α	α''	309	21.2	79.9	Cup-cone.
225	do	5,000 min. at 900° C	α	α''	246	18.0	69.5	Do.
226	do	10,000 min. at 900° C	α	α''	293	18.9	76.5	Do.

α—Body centered cubic (alpha) phase. α''—Martensite structure.

The above table shows that samples treated in accordance with Process A give clear indications of high ductility by all measures of that property. All samples shown in Table I were readily cold rolled to sheet form.

In another heat treating cycle in accordance with this invention and corresponding to curve B of the drawing the alloy sheet is annealed at a first temperature above the two-phase region, thereafter the sheet is rapidly cooled by removing the billet to a second furnace at a lower temperature, for example, to a second temperature above the lower limit of the two-phase region and at least 150° C. lower than said first temperature, the sheet is then annealed at the second temperature for at least about 5 minutes, and then is quenched rapidly in a medium below room temperature to obtain a fine grain structure having a high proportion of martensite therein.

The second process for obtaining a ductile cobalt-iron-vanadium alloy is based upon the introduction of excess vacancies or immobile dislocations in the alloy structure so as to inhibit cleavage fracture. This is accomplished by a two-step quench by means of which excess vacancies are effectively quenched in to form the immobile dislocations which suppress cleavage fracture. The immobile dislocations also serve as nuclei for subsequent martensitic transformation. The greater the number of these nuclei present, the finer the grain structure, and hence, the more ductile the alloy. Thus, the two-step quench produces a fine-grained martensitic type structure which is highly ductile at room temperature. One such successful process is set forth immediately below:

PROCESS B—(GRAPHS B OF THE FIGURE)

(1) Anneal the hot worked alloy at temperatures above the upper limit of the two-phase field. The annealing time should be sufficient for a thorough heating and substantial complete transformation to gamma phase.

(2) Cool the alloy rapidly to temperatures at least 150° C. lower and yet above the lower limit of the alpha plus gamma field. Hold the alloy at this temperature for a period of at least 5 minutes. This latter temperature may be either above or within the two-phase region, see graphs b_1 and b_2 of B in the figure.

(3) Cool the alloy as fast as possible, preferably by quenching into ice water or brine.

In Table II samples heat treated in accordance with the second process at various annealing temperatures are set forth. Sample 233 was annealed at 1100° C. for 20 hours, cooled to 920° C., held 10 minutes and then quenched. Sample 234 was annealed at 1200° C. for 20 hours, cooled to 920° C. and held ten minutes at that temperature and then quenched. Sample 235 was annealed at 1250° C. for 40 hours, cooled to 920° C., held 10 minutes at that temperature and then quenched. Samples 291 and 292 show results obtained by process b_1 of Graph B in which both anneals required by the process are carried out above the two-phase region.

Table II

Sample No.	Heat treatment	Microstructure		True stress at fracture, p.s.i.×10^3	Elongation, percent	Reduction of area, percent	Fracture mode
		Matrix	High temp. precip.				
233	1,100° C./20 hr.; 920° C./10 min.; quench	α''	$\alpha(<1\%)$	246	12	67.8	Cup-cone.
234	1,200° C./20 hr.; 920° C./10 min.; quench	α''	$\alpha(<1\%)$	223	11.7	62.6	Do.
235	1,250° C./40 hr.; 920° C./10 min.; quench	α''	$\alpha(<1\%)$	286	16.7	76.3	Do.
291	1,250° C./1 hr.; 1,050° C./8 min.; quench	α''		211	15.9	69.8	Do.
292	1,250° C./4 hr.; 1,050° C./5 hr.; quench	α''		220	13.8	75.3	Do.
232	1,000° C./20 hr.; 920° C./10 min.; quench	α''	$\alpha(<1\%)$	100	0.7	2.3	Intergranular.

α—Body centered cubic structure. α''—Martensitic structure.

It is thus seen that highly ductile materials can be produced by the second process of this invention. By contrast, sample 232 which was annealed at 1000° C. for 20 hours then cooled to 920° C. (less than 100° lower), held there for 10 minutes and then quenched, has relatively coarser grains and is a highly brittle material.

Certain precautions should be taken in employing the processes of this invention and these are enumerated below.

(1) Hydrogen, if present in any appreciable amount, should be pumped out of the alloys under vacuum at appropriate temperatures; otherwise hydrogen will produce fatal intergranular embrittlement in cobalt-iron-vanadium alloys.

(2) Oxygen should be kept as low as possible because excess oxygen also causes grain boundary embrittlement.

(3) With respect to Process A, grain boundary precipitation, particularly in the form of a continuous network, is detrimental to the ductility of the alloys and, therefore, should be avoided.

(4) In general, excessive grain coarsening should be avoided.

The two processes previously described are the preferred embodiments of the invention, but they do not exhaust the applications of this invention. Two additional processes of the invention are described below. The following process is useful, but for reasons which will be set forth, is somewhat less advantageous than the processes already detailed.

PROCESS C

This process (Graph C of the figure) requires that the alloy be annealed at a temperature above the two-phase region, and then, immediately thereafter, annealed at a temperature in the two-phase region for a length of time which is sufficient to achieve substantially equilibrium conditions in the alloy. The time of holding at the annealing temperature in the two-phase region is very important and usually is very long, being at least 48 hours.

As an example of this process a 49% iron-49% cobalt-2% vanadium alloy was annealed at 1000° C. for one hour, rapidly cooled to 920° C., held at that temperature for 167 hours, and then quenched to 0° C. Certain of the mechanical properties obtained are as follows:

Table III

Sample No.	Microstructure		True stress at fracture p.s.i.×10^3	Elongation, per-cent	Reduction of area, per-cent	Fracture mode
	Matrix	High temp. precip.				
212	α''	$\alpha(55\%)$	222	16.9	70.1	Cup-cone.

It is clear that a very ductile magnet alloy may be made in this fashion, but the long times required for the process are a serious disadvantage for commercial application.

The following process is useful for producing ductile cobalt-iron-vanadium magnetic alloys, but is not as consistently effective as those already described.

PROCESS D

This process (Graph D of the Figure) produces the desired ductility by relying on a single-phase structure, i.e., martensite, obtained by a rapid quench from a temperature above the two-phase region to a temperature below room temperature. In the following example the alloy was annealed at 1060° C. for one hour, and then quenched to 0° C.

Table IV

Sample No.	Microstructure		True stress at fracture p.s.i.×10^3	Elongation, per-cent	Reduction of area, per-cent	Fracture mode
	Matrix	High temp. precip.				
203	α''		170	10.7	42.5	Cup-cone.

Clearly, this process, too, has produced a material having good ductility. This process is highly sensitive to contaminants such as hydrogen, oxygen and carbon, however, and therefore, additional precautions to minimize the amount of these contaminants must be taken to use it successfully. As little as 20 parts per million of oxygen in the material adversely affects this process.

With respect to the various heat treatments discussed throughout this specification, it will be understood that the length of time a particular body of alloy is held at temperature will depend to a large extent upon the dimensions of the body. Massive alloy bodies will naturally require a longer time at temperature than light, thin pieces.

While efforts are made to achieve high purity in these alloys by using raw materials of high purity and vacuum melting, nevertheless small amounts of elements such as manganese (perhaps as much as .005%), nickel (perhaps .0005%), chromium, oxygen, nitrogen, sulfur, and phosphorus may be present in these alloys.

It will be understood that the above specification and drawing are exemplary and not in limitation of the invention.

I claim as my invention:

1. A heat treatment process capable of developing a highly ductile microstructure in an alloy member whereby the alloy member may be readily cold-worked to sheet form and thereafter heated treated to develop good magnetic properties, the alloy consisting essentially of, by weight, from 0.5% to 4% vanadium from 30% to 70% cobalt, and the balance iron except for small amounts of incidental impurities, the steps comprising, annealing the alloy member at a temperature above the two-phase region, air cooling the member to ambient temperature to produce a fine-grain two-phase structure, reheating the member to a temperature in the two-phase region for at least 50 minutes, and quenching the alloy member in a medium at a temperature below room temperature to obtain a fine-grain microstructure having a high proportion of martensite therein.

2. A hot working and heat treatment process capable of producing a highly ductile miscrostructure in a magnetic alloy member whereby the alloy member may thereafter be readily cold-rolled, the alloy consisting essentially of, by weight, from 0.5% to 4% vanadium, and the balance substantially equal amounts of iron and cobalt except for small amounts of incidental impurities, the steps comprising, hot working the alloy member at a temperature above the two-phase region, cooling the member to room temperature to produce a fine-grain two-phase structure comprising alpha phase and martensite, reheating the member to a temperature in the two-phase region for at least 50 minutes to transform the alpha phase to alpha plus gamma phase, and quenching the alloy member in a medium at a temperature below room temperature whereby the gamma phase is transformed to martensite to obtain a fine-grained microstructure having a high proportion of martensite therein.

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