July 2, 1968 H. L. B. GOULD ET AL 3,390,443

MAGNETIC MATERIAL AND DEVICES UTILIZING SAME

Filed Oct. 20, 1964 2 Sheets-Sheet 1

FIG. 1A

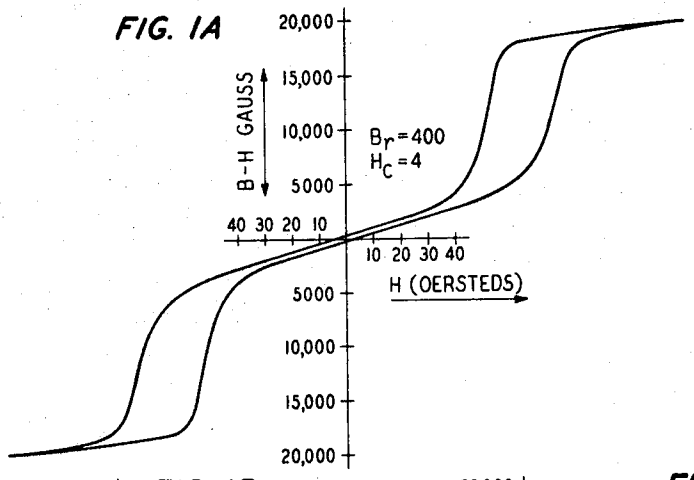


FIG. 1B

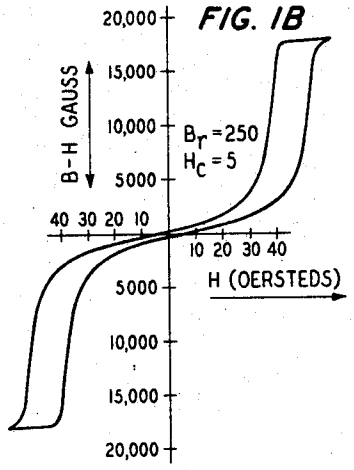


FIG. 2

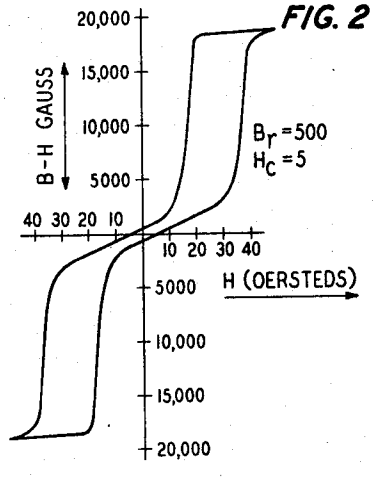


FIG. 3

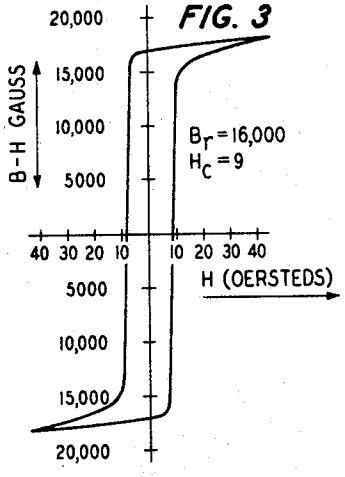
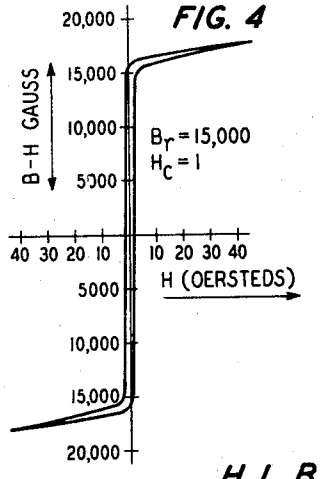


FIG. 4



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MAGNETIC MATERIAL AND DEVICES UTILIZING SAME

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FIG. 5

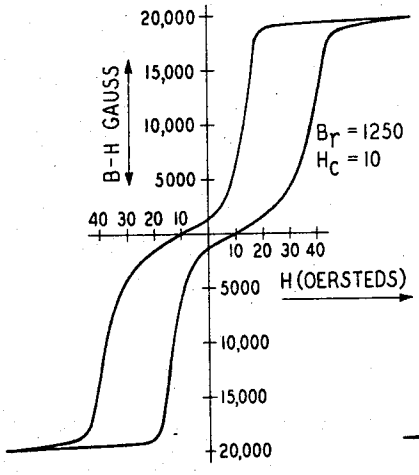


FIG. 6

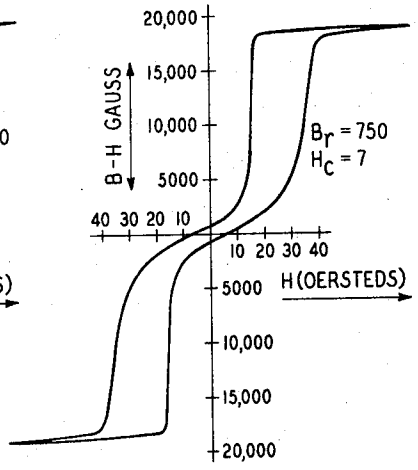


FIG. 7

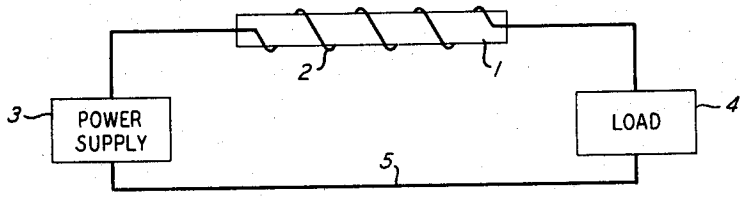
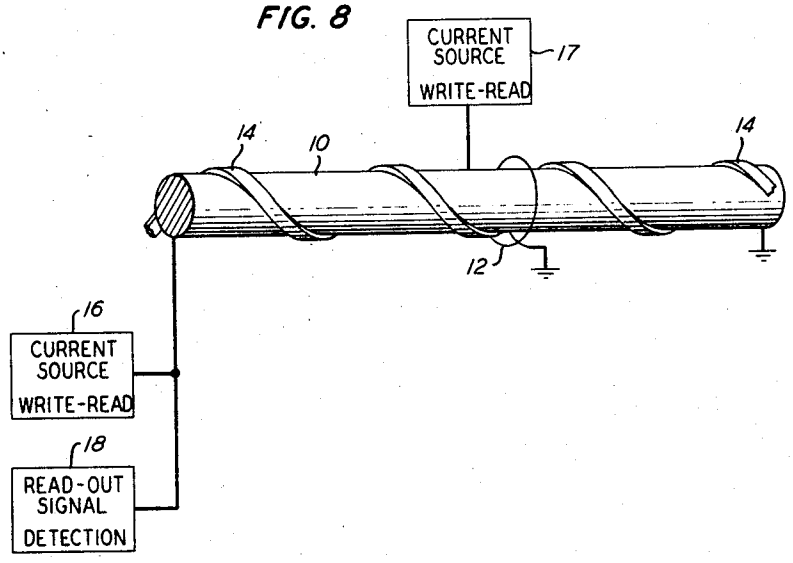


FIG. 8



United States Patent Office 3,390,443 Patented July 2, 1968

3,390,443

MAGNETIC MATERIAL AND DEVICES UTILIZING SAME

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10 Claims. (Cl. 29—180)

ABSTRACT OF THE DISCLOSURE

High cobalt-iron alloy material formed into tape by cold roll flattening, sometimes followed by annealing manifests a variety of novel magnetic properties previously unassociated with alloys in this system. The stable split hysteresis loop associated with any of the included compositions under specified processing conditions is the first to be observed in an alloy system.

This invention relates to processes for making magnetic alloy materials, to the materials themselves, and to devices containing such materials.

There are previous literature references to a unique magnetic D-C hysteresis loop configuration variously described as "split" or "wasp-waisted": 34 Electrical Engineering, 1292 (1935) and 29 Siemens Zeitschrift, 434 (1955). This loop form may be regarded as two separate biased subloops, one in the first and the other in the third quadrant, these sections being connected by a narrow, sometimes approximately linear, portion. Materials manifesting this characteristic, show a significant high induction which approaches saturation magnetization, B_{sat}, and which may initially decrease only gradually upon reversal and decrease in value of the applied field, manifest an increasing permeability before the applied field reaches zero, so that the true remanent magnetization, B_R, may be a very small value compared to B_{sat}. Such constricted loops have been found in an alloy system and in a ferrite composition. Up to now these characteristics have not been pronounced and have disappeared at high magnetizing forces.

Processing of the compositions of this invention in accordance with a particularly critical schedule may result in an extremely pronounced constricted or split loop which, in appearance, approaches two biased square loops, again one in the first and one in the third quadrant, again connected by a linear region which, in this instance, shows an extremely sharp change in permeability at a well-defined value of applied field. This characteristic, where it is produced in accordance with the conditions herein, is stable at high magnetizing fields.

Subsequent treatment of these materials, again in accordance with a critical schedule, may result in conversion of the split loop to a conventional four-quadrant square hysteresis loop of the form associated with materials now in use in magnetic switches and magnetic memory elements. As is described, variations in subsequent treatment conditions may result in a significant range of coercivities.

Square loop materials in accordance with this invention may, of course, be incorporated in any of a host of conventional devices. Technological importance is premised on high squareness values, B_R/B_{sat}, and on coercivity and saturation values which may differ from available materials and may more nearly fill the particular needs for a given family of devices. Since stable constricted loops of the pronounced characteristics associated with these materials have not been available; in fact, since there was no basis for an expectation that such characteristics would ever be available, there are few devices at this time which may take advantage of the properties. Availability of the stable constricted loop has already stimulated development of several devices which may utilize such materials. As the information becomes more generally available, it is to be expected that more uses will emerge. Probably the most significant device thus far developed is a current limiter which takes advantage of the pronounced change in permeability with applied field.

In accordance with this invention, there is described a set of processing conditions to be utilized in the manufacture of a flat tape configuration of any of a series of cobalt-iron alloys.

Suitable processing necessarily includes cold rolling, so as to result in a minimum of a 90 percent thickness reduction where such reduction is expressed as the fraction:

$$\frac{t_1-t_2}{t_1}$$

where t_1 and t_2 are the thickness of the body before and after cold rolling, respectively. While this cold rolling results in a constricted hysteresis loop regardless of prior treatment, it will be seen from the results set forth in this disclosure that subsequent partial annealing up to a temperature of the order of 500° C. increases the "squareness ratio" of the two subloops. Such treatment constitutes a preferred embodiment of this invention.

Another embodiment of the invention is realized upon heat treatment at temperatures in excess of about 500° C., such subsequent treatment resulting in a conventional four-quadrant loop. Increasing the heat treatment temperature above this minimum of about 500° C. results in decreasing coercivity over a predictable range of from about one to about 12 oersteds.

Compositions showing these properties are members of the cobalt-iron alloy system and include the range expressed in weight percent of 78 to 95 cobalt, remainder iron, to which certain additives may be made. The most significant of these additives is vanadium, an optional inclusion, which may be incorporated in amounts of up to four per cent by weight based on the entire composition. Vanadium inclusion over this range improves workability, increases resistivity, improves squareness ratio, and may result also in a small increase in coercivity. For these reasons a minimum vanadium content of one per cent is preferred. The upper limit of four percent is, however, critical, significantly greater amounts resulting in a loss of the loop characteristics described. The cobalt limits are determined by the unfeasibility of cold working resulting compositions above the indicated maximum and by the loss of the split loop characteristic below the indicated minimum. A preferred compositional range for cobalt extends from 85 to 92 weight percent. Other inclusions, both accidental and intentional, are discussed further on. All such additional ingredients are conventional and serve recognized purposes.

Reference is made to the drawing, in which:

FIGS. 1A and 1B are D-C hysteresis loops on coordinates of magnetization, B, in gauss on the ordinate and applied field, H, in oersteds on the abscissa for a material herein having constricted loop characteristics;

FIG. 2 is a similar plot for such a material after subsequent treatment;

FIG. 3 is such a plot for a material in accordance with this invention processed so as to have a conventional four-quadrant hysteresis loop;

FIG. 4 is such a plot for a material similar to that plotted on FIG. 3 but processed so as to have reduced coercivity;

FIG. 5 is again a plot on coordinates of B and H in the units indicated for a material having a constricted hysteresis loop;

FIG. 6 is a simi'ar plot for another material;

FIG. 7 is a front elevational view of a device utilizing a material herein having a constricted hysteresis loop characteristic, together with associated circuitry; and

FIG. 8 is a front elevational view of a device utilizing an element of a material herein having a conventional D-C hysteresis loop.

Detailed discussion of FIGS. 1 through 6 forms a part of the similarly numbered examples. Before proceeding to the examples, all of which refer to specific processing conditions, a general description of the processing to be followed in the attainment of either of the hysteresis loop characteristics is presented.

It has already been noted that the critical treatment is the rolling step carried out cold, carried out subsequent to any dead anneal or at least not followed by any dead anneal, and of such nature as to result in a thickness reduction of at least 90 percent, as described. However, since final desired configurations are often of relatively small dimensions, the general description which follows discusses expedient techniques for reducing the initial body of alloy material to a size which may be handled with ease on appropriate commercial equipment designed to be utilized in the final cold working. For this reason, description of the processing schedule prior to cold rolling is to be considered as exemplary only and merely suitable for the particular starting body, for the available apparatus, and for the final dimensions desired. Other desired configurations may eliminate the need for any initial processing or may result in the use of entirely different working techniques. Also, for ease of fabrication, much of the initial processing utilizes hot working. This is the conventional approach used by metallurgists in this field. These hot working techniques, while they represent the most expedient approach to the initial reduction steps, are in no way required to attain the characteristics described. They may, for example, be replaced in their entirety by cold working, or they may be eliminated.

In the experimental results reported herein, starting bodies were generally produced by casting, the cast ingot being of the order of three-quarters of an inch in diameter by eight inches in length. Other crystallizing techniques, such as zone melting or Bridgeman or crystal pulling, are suitable.

The casting was then hot worked by rolling to a thickness of the order of 0.10 inch. Hot working to produce strip, whether by either of the techniques mentioned or by any alternative procedure, as by forging, is expediently carried to a minimum thickness of the order of one-eighth of an inch.

Again, primarily as an expedient to insure a good quality surface of the final strip, surface defects were removed by milling. Alternative techniques include pickling, blasting, etc.

The hot worked strip was then subjected to a dead anneal. Requisite conditions for dead annealing in this alloy system are well known. In general, heating within the range of from 750° C. to 1000° C. for from one hour to fifteen minutes is necessary. Deviation may be made from these limits where the bulk of the body so indicates. Small strip samples may be annealed more quickly; large reels may require greater duration. In the work reported in this description, a one-hour anneal at a temperature of about 975° C. was found suitable. Annealing was carried out in a protective atmosphere of hydrogen, nitrogen, argon, helium, or forming gas (mixture of nitrogen and hydrogen). Use of a protective atmosphere is recommended to minimize the embrittling effect of oxygen inclusion. As indicated, annealing is an expedient step designed to expedite subsequent working and is not required to develop the magnetic characteristics reported.

The critical step of cold rolling was then carried out,

conditions being such as to result in a minimum 90 percent thickness reduction as determined from the fraction:

$$\frac{t_1-t_2}{t_1}$$

where t_1 and t_2 are the thickness of the body undergoing processing in the direction subject to reduction by rolling before and after rolling respectively. Preferred reductions are greater and range from 95 percent up to 99 percent and greater.

As will be seen from the examples and the accompanying figures, while the body so cold processed shows properties of value in device applications, these properties may be altered so as to make the constricted characteristic more pronounced by partial anneal. Such partial anneals are carried out at a temperature of at least 150° C., this being the lowest value at which any appreciable effect is noted for any reasonable heating time, and up to a maximum of about 500° C. Heat treatment is typically carried out over a time interval of up to about three hours. While such treatment may be continued, significant further improvement is not noted. Further, since higher temperature may result in shorter required heating times, it is generally expedient to operate over the upper end of this range, at which shorter times may suffice.

Heat treatment above 500° C., to about 550° C., may be permitted where it is desired to retain the constricted characteristic. It has been found that such treatment may be tolerated for cobalt inclusions of from 78 to 90 weight percent. Above this temperature for any of the compositions herein, and above 500° for compositions containing from 90–95 weight percent cobalt, the constricted characteristic is replaced by a conventional four-quadrant loop. The coercivity of materials evidencing the traditional characteristic may be tailored by selecting the proper temperature over the permited range of up to about 1200° C. Higher temperatures to the melting point of the alloy may be tolerated in principle. The maximum indicated is however a practical limit largely based on commercial furnace considerations. Heating times required over the higher range of from about 500 to about 1200° C., except for the lower cobalt compositions where the range commences at 550° as noted, may again range up to about three hours, the minimum requirement being that heating be continued for such period as to maintain the body at a temperature above the indicated minimum for a period of at least 15 minutes. Increasing temperature results in decreasing coercivity. For these compositions, the minimum coercivity is approximately one oersted, corresponding with a temperature of about 1200° C. The maximum attainable is approximately 12 oersteds, corresponding with the appropriate minimum temperature of 500 or 550° C.

Specific processing conditions resulting in the characteristic shown on the figures are set forth in the following examples.

Example 1

A melt was prepared of the following materials:

Cobalt—1448 grams, or 90 weight percent
Iron—150 grams, or 9.4 weight percent
Manganese—8 grams, or 0.5 weight percent
Aluminum—1.6 grams, or 0.1 weight percent.

The materials were reacted at a temperature of approximately 1550° C. The resulting melt was held at temperature for about two minutes to ensure thorough mixing and solution of ingredients, and was then poured into a mold and solidified to make an ingot about three-quarters of an inch in diameter and eight inches in length. The ingot was heated to a temperature of 1200° C. for hot rolling to a flat strip of a final thickness of 0.1 inch. Attainment of this final thickness required about 10 steps, with 3 reheatings. The strip was examined and any surface defects were removed by machining. It was then annealed for an hour at a temperature of 1000° C. in a pro-

tective atmosphere of hydrogen. The rolling was then continued cold without reheating or annealing to obtain the requisite minimum of 90 percent thickness reduction. Test samples were taken from the strip at thicknesses of 0.001 inch and 0.00025 inch, representing cold reductions of 99 percent and 99.75 percent. Conventional D-C hysteresis loop measurements resulted in those depicted in FIGS. 1A and 1B, respectively.

The constricted loop of FIG. 1A is characterized by a relatively narrow section, with a substantially constant permeability of about 100 (dB/dH) extending to magnetizing forces of about 35 or 40 oersteds. With further increase of the magnetizing force to 70 or 80 oersteds, there is a ten-fold increase in permeability, to approximately 1000. The loop then levels off and remains flat to magnetizing forces up to 400 to 500 oersteds. On the reverse of the cycle, with decreasing magnetizing force, there is a section of substantially constant low permeability of a value of about 10 extending down from 90 to about 70 oersteds. There is then an abrupt change of slope, with the permeability increasing ten-fold to 1000 for magnetizing forces of 60 down to 50 oersteds, and finally another change in slope to low constant permeability of about 10 for magnetizing forces of 30 oersteds to about zero. The characteristics of the material, measurement of which yielded the loop of FIG. 1A, may be summarized as follows. Coercive force, H_c equals 4 oersteds, residual induction Br equals 400 gauss, and the induction, B at an H of 60 to 80 oersteds equals 18,000 gauss.

TABLE 1

Cycle	Magnetizing force H in oersteds	Permeability, μ
Increasing H	0–40	100
	70–80	1,000
	80–90	10
Decreasing H	90–70	10
	60–50	1,000
	30–0	100

For the loop characteristics shown in FIG. 1B, corresponding with a material cold rolled to a thickness reduction of 99.75 percent, the loop characteristics may be summarized as follows: Coercive force, H_c, equals 5 oersteds; residual induction, B_R equals 250 gauss; induction B at H of 40 to 60 oersteds equals 18,000 gauss.

TABLE 2

Cycle	Magnetizing force H in oersteds	Permeability, μ
Increasing H	0–30	75
	40–50	1,100
	50 and over	100
Decreasing H	80–40	100
	40–30	1,100
	30–0	75

Example 2

The composition of Example 1 was processed as there described so as to result in a 99 percent thickness reduction, after which the tape was heat treated at 450° C. for one hour. The D-C hysteresis loop of FIG. 2 was measured on the heat-treated material. Comparing the characteristics of the unheat-treated material of FIG. 1A and the heat-treated material of Example 2, it is seen that the constricted nature of the loop was not changed. The main effect was to broaden and bring the subloops closer to the ordinate axis.

Example 3

Again, the composition of Example 1 was processed as there described so as to result in a thickness reduction of 99 percent (FIG. 1A), following which the tape was annealed at 600° C. for one hour. The hysteresis loop of FIG. 3 resulted. It is seen that this heat treatment condition resulted in disappearance of the constricted loop and substitution of a conventional four-quadrant loop. For these conditions, this loop has a residual induction or remanent magnetization, B_R, of 16,000 gauss, a coercive force of 9 oersteds, and a squareness ratio, B_R/B_{sat}, of 0.85, B_{sat} is the saturation point magnetization again expressed in gauss.

Example 4

Again, the composition of Example 1 was processed as there described to result a thickness reduction of 99 percent, following which the resultant tape was annealed at 1200° C. for one hour. The resulting loop, FIG. 4, shows a significantly reduced coercivity as compared with the similarly treated material of Example 3 (FIG. 3), which was heat treated at the lower temperature of 600° C. This material had a remanent magnetization, B_R, of 15,000 gauss, a coercivity, H_c, of one oersted, and a squareness ratio, B_R/B_{sat}, of 83 percent.

Example 5

The procedure of Example 1, including the final cold rolling step resulting in a thickness reduction of 99 percent, was repeated utilizing the following amounts of the indicated materials:

Cobalt—1360 grams, or 85 weight percent
Iron—230 grams, or 14.4 weight percent
Manganese—8 grams, or 0.5 weight percent
Aluminum—2 grams, or 0.1 weight percent.

The resulting strip was annealed for two hours at 480° C. The measured D-C hysteresis loop for this material is reproduced as FIG. 5.

Example 6

The procedure of Example 1, including the final cold rolling step resulting in a thickness reduction of 99 percent, was repeated utilizing the following amounts of the indicated materials:

Cobalt—1365 grams, or 85.3 weight percent
Iron—195 grams, or 12.2 weight percent
Vanadium—32 grams, or 2 weight percent
Manganese—8 grams, or 0.5 weight percent.

The resulting strip was heat treated for two hours at 500° C. The measured D-C hysteresis loop for this heat-treated material is reproduced as FIG. 6. The difference between the D-C characteristics of the materials of this example and Example 5 resulted largely from the inclusion of vanadium. The effect was generally to produce a squarer subloop in each of quadrants **1** and **3** and to steepen the slope of the portion of the loop representing the reverse cycle in quadrant **1**, as well as that of the corresponding portion of the third quadrant loop. The vanadium inclusion resulted also in a three-fold increase in resistivity to a value of about 27 micron-centimeters.

Examples 1 through 6 above were selected to represent similar working conditions and final configurations, generally with only one significant variation in composition or condition to permit ready comparison. These examples all represent actual commercial conditions and compositions. Conditions include the use of hydrogen as a protective atmosphere. Forming gas (a mixture of nitrogen and hydrogen), nitrogen, argon, or helium may be substituted. Manganese, usually included in amounts of from one-half to one percent by weight, is intended to combine with any sulfur that may be present in commercial-grade material. Suitable alternatives include beryllium, magnesium, calcium, etc. Aluminum or some other readily oxidizable element, typically in the amount of one-tenth to one percent, is sometimes included to control oxygen. Unintentional ingredients include carbon, from about one-quarter to one percent, beyond which workability is impaired, silicon, up to about two percent, larger amounts again impairing workability, molybdenum, chromium, titanium, niobium or tungsten up to about five percent (molybdenum, chromium, titanium, niobium or tungsten may be added intentionally since either of these may be substituted for vanadium for the purposes noted) and phosphorus and sulfur, to about one-tenth of one

percent, either of these last ingredients causing embrittlement in larger quantities. The total content of metallic ingredients other than those normally included should not exceed six percent.

The device of FIG. 7 is a current limiter including a core 1 of a constricted loop composition herein, which may be fabricated to the form shown by use of one or more flat strips, having wrapped about it several turns of wire 2, the extremities of which are connected, one to D-C source 3, the other to load 4. The circuit is completed by wire 5 connecting power source 3 and load 4. Such a series-connected element, utilizing, for example, the material of FIG. 2, depends for its operation on the fact that the impedance presented to currents producing magnetomotive forces up to about 40 oersteds is relatively small by reason of the low linear permeability portion of the hysteresis loop. Beyond this value there is a steep increase of about ten-fold to a permeability value of about 1000 proportionally increasing the inductance and correspondingly the impedance to current.

The device of FIG. 8 is a memory element known as the twistor. This device, which depends upon the direction of remanent magnetization of a length of magnetic tape (a memory bit) for information, is fully described in U.S. Patent 3,083,353, issued Mar. 26, 1963 to A. H. Bobeck. This device includes a metallic conductor 10, about which there is disposed a helical winding 14 of a tape configuration of a composition herein. The direction of the flux in the winding 14 may be in either of the helical directions. One end of the conductor 10 is connected to a current source 16 and the other end is connected to ground. A series of external insulated windings represented by 12, one end of each of which is connected to ground, the other end being connected to a current source 17, are inductively coupled to the conductor 10. Initially, all the bits, that is sections, of winding 14 corresponding with windings 12, are magnetized in a given direction, with such direction representing, for example, a binary zero. To switch any given bit, it is necessary to generate a current sufficient to produce a magnetomotive force, H, to produce an opposite flux direction. When a current pulse producing a magnetomotive force of the magnitude $H/2$ is applied from the source 16 simultaneously with a current pulse again producing a magnetomotive force of the magnitude $H/2$ from a given source 17, the total magnetomotive force is sufficient to switch the flux state of the associated length of winding 14, so producing a binary 1. In accordance with the principles of coincident current memory elements generally, either of the current pulses applied from the sources 16 and 18 alone is insufficient to accomplish the magnetic switching.

Information stored in the winding 14 is read out by reversing the polarity of the currents applied from the sources 16 and 17, the simultaneous reverse current pulses again causing switching in the direction of magnetization in the helical winding if a binary "1" has been previously stored in the manner described above. No switching occurs for any bit magnetized in the zero direction. When the magnetic state of the winding 14 is switched during the read function, a change in potential results. This change may be detected by suitable detection means 18 as an output pulse superimposed upon the switching current pulse.

The invention has been described in terms of a limited number of examples. In general, all such information has been selected with a view to simplicity of comparison and to demonstrate rather than to limit device applicability. The invention is truly limited only by the compositional ranges and processing ranges indicated, the latter of which is to be considered as particularly critical. Materials of this invention are necessarily processed only by cold rolling so as to result in a thickness reduction of at least 90 percent. Other techniques have not been found to have equivalent results. Within these limits the invention should be considered as embracing constricted loop and square loop materials, however produced and however utilized.

What is claimed is:

1. Device comprising a ferromagnetic body of an alloy consisting essentially of 78 to 95 weight percent cobalt, 0 to 4 weight percent vanadium, remainder iron, produced by cold rolling so as to produce a thickness reduction of at least 90 percent based on the ratio:

$$\frac{t_1-t_2}{t_1}$$

where t_1 and t_2 are the thickness of the body in that dimension subject to reduction in the rolling operation, before and after rolling, respectively, the said body having associated therewith at least one electrical current path so situated that passage of current through the said path results in a magnetic flux within at least a portion of the said body.

2. Body of claim 1 in which the said alloy consists essentially of from 85 to 92 weight percent cobalt.

3. Body of claim 1 in which the said alloy contains at least one percent vanadium.

4. Body of claim 1 in which the said body is heat treated after rolling at a temperature of from 150 up to 500° C. for alloys containing from 90 to 95 weight percent cobalt and from 150 up to 550° C. for alloys containing from 78 to 90 weight percent cobalt.

5. Device of claim 1 in which the said body is heat treated after rolling at a temperature of from 500 to 1200° C. for alloys containing from 90 to 95 weight percent cobalt and from 550 to 1200° C. for alloys containing from 78 to 90 weight percent cobalt.

6. A device as in claim 1 subjected to heat treatment at a temperature of up to 1200° C.

7. Device of claim 1 in which the said electrical current path consists of at least one turn of conductive wire about the said body.

8. Device comprising a body of material defining at least one magnetically remanent flux path, the said body comprising an alloy consisting essentially of 78 to 95 weight percent cobalt, 0 to 4 weight percent vanadium, remainder iron, produced by cold rolling so as to produce a thickness reduction of at least 90 percent based on the ratio:

$$\frac{t_1-t_2}{t_1}$$

where t_1 and t_2 are the thickness of the body in that dimension subject to reduction in the rolling operation before and after rolling, respectively, such body having associated therewith at least two electrical paths.

9. A device as in claim 8 subject to heat treatment at a temperature of up to 1200° C.

10. Device of claim 8 in which the said body constitutes a helical winding about a metallic member, the said member representing one of the said current paths.

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