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PROCESSING MAGNETIC MATERIAL

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This invention relates to a process for producing ductile magnetic alloys and in particular to the heat treatment for producing substantially pure iron-cobalt magnetic alloys in a ductible condition.

In the past there have been a number of soft magnetic alloys which have been developed to provide an optimum combination of magnetic properties. Among these, an alloy known in the trade as 2V Permendur is noteworthy in that it is characterized by the highest operating magnetic induction, the highest Curie point and the highest magnetostriction of any of the commercially available soft magnetic alloy core materials. Recently, a variation of Permendur has been announced consisting of a substantially pure alloy comparing about 2% vanadium, 49% cobalt and 49% iron. This substantially pure magnetic alloy is known to the trade as "Supermendur." It is characterized by having a total impurity content of less than 0.10% impurities and, when properly processed, has the lowest coercive force, the lowest hysteresis loss, the highest maximum permeability, the highest permeability associated with the highest flux density, the highest remanence, and a rectangular hysteresis loop with the greatest flux swing from minus remanence to plus saturation, as compared with other known and commercially available soft iron-cobalt magnetic alloy core material. However, these magnetic properties can only be obtained when the alloy is made from proper raw materials and is subjected to the proper processing.

In the normal mill processing of the commercially available Permendur, the hot rolled material is annealed at a temperature of about 1670° F. and quenched in ice water to obtain a malleable structure suitable for cold rolling. Since the chemical composition of Supermendur varies from the chemical composition of Permendur essentially only in the impurity content present in the alloys, it was believed that the heat treatment applied to Permendur would be effective when applied to Supermendur for producing a structure which would permit subsequent cold rolling to the final gauge. Experience has shown, however, that such is not the case; Supermendur, who so processed, became extremely brittle and cracked upon normal withdrawal from the furnace into the quenching medium.

An object of this invention is to provide a process whereby substantially pure iron-cobalt soft magnetic alloys can be heat treated to obtain a malleable structure.

Another object of this invention is to provide a process in which substantially pure iron-cobalt soft magnetic alloys can be processed on a commercial scale.

A more specific object of this invention is to provide a process for commercially treating substantially pure iron-cobalt-vanadium soft magnetic alloys to obtain the highest maximum permeability associated with the low coercive force and hysteresis loss.

Other objects of this invention will become apparent from the following description:

In a broad sense, the process of this invention relates to the substantially pure iron-cobalt alloys to which small amounts of other elements such as titanium, chromium or vanadium may be added, an example of which is the alloy known as Supermendur and which has a composition within the range between 1.5% and 2.5% vanadium, 45% and 52% iron and 45% and 52% cobalt with not more than 0.10% incidental impurities exclusive of nickel which may be present in an amount up to 0.4% as will be referred to hereinafter. In this type of alloy, it is necessary that the highest purity be obtained in the final chemical analysis of the alloy. Presently this is accomplished by vacuum melting high purity vanadium, electrolytic iron, and electrolytic cobalt.

It is to be noted that despite the use of extremely pure components certain other elements are normally present within the alloy, Supermendur. Thus even by employing electrolytic cobalt as the source of cobalt in the present alloy, the resulting alloy may contain nickel in an amount of up to 0.4%. It is not economically feasible to remove the minute amount of nickel from the cobalt by any known commercial means; however, in this particular alloy, this minute amount of nickel, that is, up to a maximum of 0.4% is not essential and may be present without adversely affecting the magnetic characteristics of the alloy to any serious degree. However, there are other elements which also appear in the final analysis of the alloy which are partially introduced through the raw materials and partially through contamination from the furnace refractories. So long as these incidental impurities, as that term is used herein are limited to 0.10% maximum, exclusive of the nickel content, the alloy is capable of exhibiting outstanding magnetic characteristics, which magnetic characteristics are vastly superior to those of the Permendur, regardless of whether each of the alloys has been subjected to a regular anneal or a special magnetic annealing heat treatment as will be set forth more clearly hereinafter. These high purity components are melted in a controlled atmosphere furnace or in a vacuum type furnace and are cast into ingots in the normal steel making manner.

After the metal has solidified and cooled to a sufficient degree, it is removed from the controlled atmosphere or vacuum furnace and thereafter cooled in air to room temperature. The ingots are then heated to a temperature in the range between 2000° F. and 2250° F. and preferably forged to disrupt and distribute the as-cast structure. It will be appreciated however, that other forms of hot working may be employed as desired. No particular difficulty has been encountered in the hot working of these alloys. Moreover, it has been found that if it is necessary to condition the initially hot worked alloy, scarfing is preferred since it has been found that grinding may have a tendency to produce hairline cracks which may cause trouble during any subsequent hot working operation.

The initially hot worked alloy can be hot rolled in the regular steel mill manner. It is preferred to heat the alloy to a temperature of about 2250° F. and complete the hot rolling operation before the material drops to a temperature below 1700° F. In practice it has been found that after forging the ingot into a slab measuring 2¾" x 4½" x 7', the slab may be conveniently hot rolled to a semi-finished mill product termed a "hot rolled band" having a thickness between 0.060" and 0.090" by heating the slab to a temperature of about 2250° F. and hot rolling directly therefrom to a hot rolled band, the finishing temperature being between 1700° F. and 1750° F. The hot rolled band must be coiled hot since during the cooling of the hot rolled band to room temperature, the alloy becomes brittle to such a degree that it cannot be coiled cold.

Subsequent to the hot rolling treatment, it is necessary to heat treat the hot rolled band in order to produce the band in a malleable condition suitable for cold working to the final gauge. In the prior art practice, as discussed in the publication "Ferromagnetism," by Bozorth, page 202, D. Van Nostrand Co., 1951, in processing Permendur the hot rolled band is heat treated by annealing at a

temperature in the range between 1550° F. and 1650° F. and thereafter quenching the iced brine. On a commercial scale, the coil of hot rolled material is placed on a reel inside of a furnace having first been joined as by welding or bolting to a stainless steel leader strip which projects out of the furnace. After annealing at 1550° F. to 1650° F. for a time period of between 4 and 16 hours, the material is withdrawn from the furnace and quenched by pulling it through a quenching tub containing iced brine. The heat treated band can be coiled and it is in a sufficiently malleable condition to withstand a great degree of cold work. Subsequent to the quenching operation, the annealed hot rolled band is surface conditioned, pickled and cold rolled to thickness of between 0.001" and 0.014" without any intermediate heat treatment..

When the above process was applied to Supermendur, it was found that the material cracked and fractured when removed from the furnace and drawn into the quenching medium. Metallographic examination indicated that the material underwent excessive grain growth. It is therefore necessary to find a means for controlling the grain growth of this material since it has been found that the material exhibiting an extremely large grain size, that is, greater than about ASTM #3, is impossible to quench to a malleable structure on a commercial scale. In this same vein, Permendur when processed in accordance with the prior art practice as set forth hereinbefore did not exhibit the extremely large grain size. Metallographic examination reveals that his may be due in part to the fact that commercially melted Permendur exhibits a large amount of inclusions which X-ray studies indicate are predominantly Al_2O_3 and V_2O_5. The total weight percentage of these inclusions in commercially melted Permendur was found to be greater than 0.10%. On the other hand, the substantially pure alloys like Supermendur to which this invention is applicable and which are made from the substantially pure raw materials have a total weight percentage of inclusions or impurities of less than 0.10% contained therein exclusive of the nickel content.

In order to more clearly demonstrate the advantages of the process of this invention, reference may be had to Table I which illustrates the composition of a number of alloys some of which fall within the range of the analysis of Supermendur, and others which fall within the range of Permendur.

TABLE I

Chemical Composition

[Weight percent]

Element	2V009	2V011	2V012	2V018	1V120	30571
C	0.010	0.006	0.007	0.004	0.006	0.030
Mn				0.005	0.002	0.67
Si	<0.01	<0.01		0.01	0.005	0.19
Cr	<.01	<.01	.01			0.01
Ni	.35	.11	.18	0.11	0.20	0.19
Al				0.01	0.008	0.01
Co	49.35	49.80	49.80	48.54	49.12	47.8
S	0.004	0.004	0.005	0.010	0.007	0.022
P	0.003	0.010	0.010	0.009	0.002	0.008
V	2.04	2.10	2.12	1.95	2.07	2.2
Cu				0.01		0.042
Fe	48.22	48.13	48.15	50.62	48.52	48.70

It is to be noted that a summation of all of the listed elements may, in some cases, total less than 100% or more than 100%. However, these variations in the experimental analyses are within the reasonable margin of error for wet chemical analyses and are relatively accurate, as that term is used, with respect to analytical chemistry.

Heat No. 2V009 was vacuum induction melted and cast into a single 9" x 9" ingot weighing 347 lbs. The ingot was heated to 2250° F. and forged to a slab measuring 2¾" x 4¾" x 7'. The slab was heated to 2250° F. and hot rolled directly without difficulty to a band measuring 4⅞" x 0.056", the finishing temperature being 1730° F. Good surface and very little edge checking was noted. The material was coiled hot and thereafter allowed to cool to room temperature.

Samples were cut from the hot rolled band of Heat 2V009 and such samples, together with samples of Permendur, the analysis of which is not reported herein, were subjected to laboratory experiments to determine the quenching temperature range that should be applied to the materials. As quenched from a temperature in the range of 1450° F. to 1700° F., both materials could be bent 180° without difficulty and exhibited hardnesses in the range from 92 R_b to 23 R_c in the laboratory quenched samples. As with past practice, it was therefore decided that a temperature of 1600° F. should be used for the annealing of this material (Heat 2V009) since it reacted on the laboratory scale in the same manner as Permendur. The hot rolled band of the Heat 2V009 material with its stainless steel leader strip was positioned within the annealing furnace and heated to a temperature of 1600° F. and held for three hours. It required six hours to heat the coil from 1115° F. to 1540° F. and the time above 1540° F. was about 17 hours. Simultaneously and in the same furnace, a regular Permendur band was also heat treated and it was withdrawn first and successfully quenched into a 10% ice brine quenching medium held at a temperature between 30° F. and 35° F. However, when the Supermendur coil was pulled from the furnace, it started to crack and broke and shattered after about 20 feet were out of the furnace. The material from the Supermendur coil was brittle and unusable for commercial processing. It was interesting to note that the Supermendur broke during and after the quench and the break did not necessarily start at the edge. Metallographic examination also revealed that the material as hot rolled had essentially the same grain size as the regular Permendur. However, it was evident that the Supermendur was much cleaner and contined far less inclusions than the regularly produced Permendur. During the mill anneal, the Permendur underwent substantially no grain growth, whereas the Supermendur developed a substantially larger grain size. It was therefore believed that the unsuccessful quenching of the Supermendur was due primarily to the large grain size.

In order to alleviate this condition and to produce a malleable structure which permits cold working to the finish gauge of the final product, this invention utilizes a heat treatment including, inter alia, preheating the alloy to a temperature in the range between about 1020° F. and 1120° F. for a time period ranging between about 3 hours and 10 hours, followed by another heat treatment, without any intermediate cooling, at a temperature in the range between 1425° F. and 1475° F. for a time period ranging between 1½ hours and 3 hours, followed by a quenching treatment to a temperature in the range between 35° F. and 50° F. after which the temperature of the alloy is permitted to raise to room temperature. Where desired, the alloy can be thereafter heated to a temperature in the range between room temperature and about the boiling point of water to aid in coiling the quenched alloy.

The necessity of preheating the essentially pure iron-cobalt alloy at a temperature within the range between 1020° F. and 1120° F. will permit the alloy to be later heated at the higher temperature without the danger of excessive grain growth. This appears to be of paramount importance in the successful quenching of Supermendur because the high purity of the metal permits rapid grain growth at the heat treatment temperature. Conversely stated, since the alloy Supermendur has less than 0.10% of incidental impurities exclusive of nickel, the alloy is

relatively free from inclusions, and since the inclusions are a great contributing factor for inhibiting grain growth at the heat treatment temperature, the absence thereof contributes to the observed phenomenon of excessive grain growth at the heat treatment temperature. It must be realized that primarily grain growth occurs during the heat treatment of this alloy. The heat treatment of this essentially pure iron-cobalt magnetic alloy requires heating to a temperature above the critical temperature of the order-disorder phenomenon which occurs at a temperature in the range between about 1290° F. and 1380° F. depending upon the composition. It has been noted that when the material is heated above the critical transformation temperature of the order-disorder phenomenon, excessive grain growth occurs which it is believed is motivated by grain boundary energies. It is thus apparent that the time at which the material is held at a temperature above the critical transformation temperature must be held to a minimum in order to minimize excessive grain growth, because the excessive grain growth appears to make it impossible to commercially quench the alloy. For this reason, it is preferred to preheat the alloy to a temperature slightly below the critical transformation temperature and the temperature at which rapid grain growth occurs and preferably at a temperature in the range between 1000° F. and 1120° F. Since no appreciable grain growth takes place at this temperature, it is preferred to hold the alloy in this temperature range until it is thoroughly soaked and preferably for a time period ranging between about 3 hours and about 10 hours. The preheating of the alloy will permit the alloy mass to be heated to this temperature range without excessive grain growth occurring, thereby minimizing the total time at which the alloy is held at a temperature above the critical transformation temperature and the temperature at which rapid grain growth occurs. It is, of course, realized that it is necessary to heat the alloy to a temperature above the critical transformation temperature in order to obtain an optimum amount of disorder which will permit the alloy to be successfully quenched to obtain a malleable structure.

Following the preheating of the alloy as set forth hereinbefore, the temperature of the essentially pure iron-cobalt alloy is raised to a temperature preferably within the range between about 1425° F. and about 1475° F. for a time period of between about 1 hour and about 4 hours. Of course, it will be appreciated that the alloy is not cooled subsequent to the preheating for such cooling would destroy the advantage gained by preheating. It is during the heat treatment at this higher temperature that the alloy undergoes the order-disorder transformation and grain growth. However, since the temperature of the heat treatment is near the lower limit of the range of temperature in which rapid growth occurs, and the time that the alloy is subjected to this temperature range is relatively short, grain growth is minimized. While lower temperatures may be employed for longer time periods or higher temperatures may be used for shorter time periods, optimum results are obtained when the temperature is maintained within the range between about 1425° F. and about 1475° F. for a time period of about 1 hour to about 4 hours. Thereafter, the alloy is quenched as will be fully explained hereinafter.

It is preferred to immediately quench the alloy from the heating temperature described in a quenching medium maintained at a temperature in the range between about 30° F. and about 50° F. This is conveniently accomplished by subjecting the alloy to immersion in a refrigerated water solution containing about 10% brine. When the alloy reaches a temperature within the range between 30° F. and 50° F., it is removed therefrom, and where desired, it is heated to a temperature in the range between about 80° F. and about 190° F. to facilitate easier coiling.

In practice, Heat 2V011, having the analysis given hereinbefore, was forged and hot rolled to a thickness of about 0.060 inch. The metal in coil form was placed in a furnace and preheated to a temperature in the range between 1000° F. and 1050° F. for a time period of about 10 hours. Thermocouple measurements indicated that the coil attained a temperature in the range between 970° F. and 990° F. for a time period of about 7 hours. The temperature was then rapidly increased to a temperature in the range between 1425° F. and 1465° F. for a time period of 2 hours. The coil was then withdrawn through a quenching medium consisting of a 10% solution of brine held at a temperature of 50° F. The coil was withdrawn at a rate of speed in the range between 165 and 248 feet per minute. Tests revealed that at room temperature the heat treated metal could be bent 180° without fracture and exhibited a hardness of between 94 R_b and 97 R_b.

Heat 2V012, having analysis given hereinbefore in Table I, was processed using the same cycle as set forth for Heat 2V011. Substantially similar results were obtained in that the metal could be bent 180° without fracture and exhibited a hardness in the range between 93 R_b and 97 R_b.

The process of this invention is effective for commercially quenching substantially pure iron-cobalt magnetic alloys without producing any adverse effect upon the magnetic characteristics thereof. The alloy after quenching, according to the process of this invention, is in a sufficiently ductile condition, such that it can be cold rolled to a thickness in the range between 0.001 and 0.014 inch in thickness. The metal, having the thickness as above set forth, is then subjected to a bright anneal in a magnetic field in order to develop the characteristics. It has been found that when the metal of Heats 2V009 and 2V011 was bright annealed at 1600° F. for 4 hours in a D.C. magnetic field of 6 oersteds and thereafter cooled at the rate of about 200° F. per hour, these steels had the following characteristics:

TABLE II

Section A

HEAT 2V009—4 MIL WOUND CORE

	1H	5H	10H
B_{max}, gausses	21,050	22,100	22,500
Br, gausses	20,550	20,700	20,740
Hc, oersteds	.196	.196	.192
Br/B_{max}	.976	.937	.922
μ_{max}	85,660		

Section B

HEAT 2V011—12 MIL WOUND CORE-MgO COATED

	1H	5H	10H
B_{max}, guasses	20,550	21,800	22,300
Br, gausses	19,550	19,800	19,800
Hc, oersteds	.176	.177	.177
Br/B_{max}	.951	.908	.89
μ_{max}	85,000		

As can be seen from Table II, the magnetic properties exhibited by the alloy are reproducible within narrow limits from heat to heat. These properties are as good as the properties reported for the metal when processed in a laboratory under exacting conditions and control.

Reference is directed to Table III, which illustrates the effect of indicidental impurities on various magnetic characteristics of these alloys.

TABLE III

Permendur Versus Supermendur; Standard Anneal Versus Magnetic Anneal Ring Samples

[Annealed at 1385° F.-4 hours PDH_2 rapid cool]

I

	Permendur	Supermendur	Supermendur	Permendur	Supermendur
Heat	30571	2V018	1V120	30571	2V018
Gauge	.014	.014	.014	.006	.006
μ_{max} from 100H	2,800	10,000	8,000	4,200	8,200
A. D.C. HYSTERESIS FROM 1H					
Bm	1,670	4,250	2,260	1,900	4,000
Br	270	2,150	920	360	2,200
Hc	.164	.403	.420	.192	.500
Br/Bm	.162	.506	.407	.189	.550
B. D.C. HYSTERESIS FROM 5H					
Bm	12,900	20,200	19,300	15,600	19,600
Br	6,700	10,200	7,100	10,200	10,200
Hc	1.72	.720	.760	1.70	.720
Br/Bm	.519	.505	.368	.654	.520
C. D.C. HYSTERESIS FROM 10H					
Bm	17,400	21,450	20,700	18,500	21,000
Br	8,600	10,050	7,000	11,100	10,100
Hc	2.09	.740	.770	1.81	.860
Br/Bm	.494	.469	.338	.600	.479
D. D.C. HYSTERESIS FROM 25H					
Bm	21,500	22,400	22,100	20,900	22,300
Br	9,400	9,800	7,200	11,500	10,000
Hc	2.24	.730	.735	1.86	.850
Br/Bm	.437	.438	.326	.550	.448
E. D.C. HYS TERESIS FROM 50H					
Bm	23,200	22,900	22,700	21,800	22,800
Br	9,600	9,800	7,100	11,600	9,800
Hc	2.26	.735	.730	1.86	.845
Br/Bm	.414	.428	.313	.532	.430

Magnetic Anneal

II

	Permendur	Supermendur
Heat	30571	2V018
Gauge	.014	.014
μ_{max} from 100H	4,200	55,500
A. D.C. HYSTERESIS FROM 1H		
Bm	2,250	21,100
Br	1,850	20,800
Hc	.360	.236
Br/Bm	.822	.986
B. D.C. HYSTERESIS FROM 5H		
Bm	13,850	21,700
Br	9,350	20,900
Hc	1.60	.234
Br/Bm	.675	.963
C. D.C. HYSTERESIS FROM 10H		
Bm	16,700	22,200
Br	12,300	21,000
Hc	1.72	.240
Br/Bm	.737	.946
D. D.C. HYSTERESIS FROM 25H		
Bm	19,900	22,700
Br	10,900	21,000
Hc	1.76	.238
Br/Bm	.548	.925
E. D.C. HYSTERESIS FROM 50H		
Bm	21,400	22,900
Br	10,800	20,900
Hc	1.76	.235
Br/Bm	.505	.913

By comparison with the chemical analyses reported in Table I hereinbefore, it will be seen that substantially the only difference between Heats 30571 and Heats 2V018 and 1V120 resides in the chemical composition of the incidental impurities, exclusive of nickel. Heat 30571 is regular Permendur, whereas the other heats are Supermendur having a maximum of 0.10% incidental impurities. Table III illustrates that the Supermendur heats exhibit outstanding magnetic characteristics in comparison with the Permendur characteristics where they have been given a standard anneal. Thus, the sole difference residing in the magnetic characteristics of these alloys is clearly attributed to the amount of incidental impurities contained therein. This comparison of the magnetic characteristics is more outstanding where these alloys have been subjected to a magnetic anneal consisting of heating to a temperature of 1400° F. at the rate of about 250° F. per hour, holding at 1400° F. for a time period between 15 minutes and one half hour and then heating to 1550° F. for four hours. Thereafter, the alloys are cooled to 1000° F. in a magnetic field of 5 amperes. Throughout the heat treatment cycle the alloys are subjected to a protective atmosphere of pure dry hydrogen. The test results in Table III clearly illustrate the outstanding magnetic characteristics exhibited by Supermendur which result primarily from the purity of the alloy.

There are no special skills or equipment utilized in practicing the process of this invention. The equipment is the same that is used in the commercial production of other iron-cobalt magnetic alloys which are currently in use. The process is effective for commercially quenching iron-cobalt magnetic alloys having an extremely high degree of purity which are characterized by being subjected to excessive grain growth when heated to a temperature above the critical transformation temperature.

This is a continuation-in-part of application Serial No. 769,561, filed October 27, 1958, now abandoned.

We claim:

1. In the processing of substantially pure iron-cobalt alloys in the form of strip to obtain a ductile alloy, characterized by the alloy containing as impurities less than 0.4% maximum nickel and less than 0.10% of other incidental elements, the steps comprising, preheating the alloy in the form of coiled strip to a temperature in the range between 1020° F. and 1120° F. for a time period ranging between about 3 hours and about 10 hours, increasing the temperature of the heat treatment until the temperature of the alloy is within the range between about 1425° F. and 1475° F., holding the alloy strip at said temperature range for a time period of between 1½ hours and 3 hours, and withdrawing the strip from the heat treating furnace through a quenching medium maintained at a temperature in the range between about 30° F. and 50° F. at a rate of between about 160 and about 300 feet per minute.

2. In the processing of substantially pure iron cobalt alloys in the form of strip to obtain a ductile alloy, the alloy being characterized by containing as impurities less then 0.4% maximum nickel and less than 0.10% of other incidental elements, the steps comprising, preheating the alloy to a temperature in the range between 1020° F. and 1120° F. for a time period ranging between about 3 hours and about 10 hours, increasing the temperature of the alloy to temperature range between about 1425° F. and 1475° F. for a time period ranging between about 1½ hours and about 3 hours, quenching the alloy in a quenching medium maintained at a temperature in the range between about 30° F. and 50° F. and thereafter heating the alloy to a temperature of up to 190° F.

3. In the processing of substantially pure iron-cobalt magnetic alloys to obtain a ductile alloy having a composition within the range between 45% and 52% iron, 45% and 52% cobalt, 1.5% and 2.5% vanadium and which is characterized by having as impurities less than 0.4% maximum nickel and less than 0.10% of other inci-

dental elements, the steps comprising, preheating the alloy to a temperature within the range between 1020° F. and 1120° F. for a time period ranging between about 3 hours and about 10 hours, increasing the temperature of the alloy to a temperature in the range between 1425° F. and 1475° F., holding the alloy at said temperature for a time period ranging between 1½ hours and 3 hours, and quenching the heated alloy in a quenching medium maintained at a temperature in the range between about 30° F. and 50° F.

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