(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 480 722 B1**

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification :
14.09.94 Bulletin 94/37

(51) Int. Cl.^{5} : **H01F 1/053**

(21) Application number : **91309316.7**

(22) Date of filing : **10.10.91**

(54) **Method of making a Nd-Fe type permanent magnetic material.**

(30) Priority : **10.10.90 GB 9022033**

(43) Date of publication of application :
15.04.92 Bulletin 92/16

(45) Publication of the grant of the patent :
14.09.94 Bulletin 94/37

(84) Designated Contracting States :
BE DE ES FR GB IT NL SE

(56) References cited :
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PATENT ABSTRACTS OF JAPAN vol. 13, no. 352 (E-801)(3700) 8 August 1989

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Description

The present invention relates to a method of making a material with permanent magnetic properties.

U.S. Patent Specification No. 4,496,395 to croat dated January, 29 1985 and assigned to General Motors Corporation of USA describes how materials with permanent magnetic properties had previously been made using samarium and cobalt (as well as other materials). The specification continues by pointing out that these elements are expensive due to their scarcity and therefore unsuitable for use in mass production of magnets. The specification then goes on to point out the known desirability of substituting lower atomic weight rare earth elements for samarium and substituting iron for cobalt, but points out that efforts to produce a permanent magnet using these materials have not been successful. Finally, the specification discloses a method of combining these elements to make a magnetic material comprising the steps of forming a mixture of iron and one or more rare earth elements; heating said mixture to form a homogeneous molten alloy; and quenching said molten alloy at a rate such that it solidifies substantially instantaneously to form an alloy having an inherent room temperature magnetic coercivity of at least about 5,000 Oersteds as quenched. The specification also discloses the product resulting from the above method.

Later U.S. Patent Specification No. 4,802,931 to Croat dated February 7, 1989 and assigned to General Motors Corporation of U.S.A. describes a novel high strength magnetic alloy made from iron, boron and lower atomic weight rare earth elements such as neodymium and praseodymium. Again the method involved consists in melting the mixture and then rapidly quenching the molten mixture.

Objects of the present invention are to provide an alternative and improved method of making a permanent magnetic material including the aforementioned less expensive and less scarce elements, and to provide an alternative and improved product.

The invention provides a method of making a material with permanent magnetic properties at room temperature comprising the steps of :-

(a) forming a mixture of iron, neodymium and other elements;

(b) heating the mixture;

(c) cooling the mixture;

characterized in that :-

(d) the elements are ground into a powder so that the mixture is formed of particles of size lees than 10 microns;

(e) the mixture comprised by atomic weight per cent approximately

not more than 50% neodymium (Nd)
not more than 4% cobalt (Co)
not more than 20% dysprosium (Dy)
not more than 15% boron (B)
not more than 12% molybdenum (Mo)
not more than 15% niobium (Nb)

the balance being iron (Fe) and impurities.

(f) the mixture is pressed into the desired finished shape before heating;

(g) the preparation of the particles, the mixing and the pressing are carried out in a low oxygen moisture free environment;

(h) heating is effected as that the temperature rises in a series of cycles each comprising a period of sharply increasing temperature followed by substantially constant temperature;

(i) heating continues until the mixture reaches sintering temperature; and

(j) the mixture cools relatively slowly.

Preferably the low oxygen environment mentioned at step (g) above is a vacuum or an inert gas environment.

The invention also provides a material with permanent magnetic properties made by the above method.

The principal advantage of the present invention over the teaching of the later Croat specification in that the resulting material has improved properties. Firstly, the material in accordance with the invention has greatly improved magnetic properties and in particular the magnetic coercivity is doubled. Secondly, the material lends itself to electroplating which prevents corrosion and greatly increases its lifespan. Thirdly, the material can withstand significantly higher temperatures. Fourthly the method lends itself to automation.

The invention will now be described more particularly by way of example with reference to the accompanying drawings in which :-

Figure 1 is a graph of temperature versus time during heating;

Figure 2 is a chart showing the characteristic of ten different magnetic materials according to the invention;

Figure 3a to 3f show magnetic and physical characteristics and demagnetization curves for six of the ten materials; and

Figure 4 is a chart comparing the properties of the material according to the invention with those of the prior art.

One specific example of a method according to the invention and the resulting product will now be described in detail. The constituents of the mixture by atomic weight per cent are :-

1)	Neodymium	(Nd)	30-35%
2)	Iron	(Fe)	60-67%
3)	Cobalt	(Co)	1-4%
4)	Dysprosium	(Dy)	1-4%
5)	Boron	(B)	0.8-1.2%
6)	Niobium	(Nb)	0.6-1.0%
7)	Aluminum	(Al)	0.4-0.8%

One or more than one of the following elements may be added, the amount of these elements is limited to not more than the value specified atomic weight percent as follows:-

Al	15%,	Bi	10%,	Cr	12%,	Ge	10%
Hf	10%,	Mn	12%,	Ni	12%,	Sb	5%
Si	10%,	Sn	5%,	Ta	15%,	Ti	8%
V	15%,	W	15%,	Zn	5%,	Pr	30%
Y	30%	Zr	10%	Mo	12%		

The above atomic elements are ground and mixed to a powder form by a jet pulveriser, the particle sizes being between one tenth and ten microns. The mixture is then pressed to form the desired final shape and is then magnetized. Grinding, mixing and pressing are carried out in a nitrogen environment. The formed shape is then heated by application of heat so that the temperature rises in the manner shown in Figure 1 until the sintering temperature is reached after which the temperature is allowed to cool naturally. Finally, the resulting permanent magnet is electroplated.

Relatively slow cooling means cooling slowly relative to the disclosure of US 4 496 395. In preferred embodiments the sintered material is cooled no faster than 75°C/min, especially no faster than 50°C/min, more especially no faster than 35°C/min.

In order to obtain the product of the invention it will generally be necessary to reduce the heat input in order to produce periods of substantially constant temperature. By way of routine experimentation based on the teaching of the instant specification the skilled worker will be able to devise suitable heat treatment regimes.

Instead of carrying out the grinding, mixing and pressing steps in a nitrogen atmosphere, they may by carried out in a vacuum or in an inert gas environment such as helium, neon, argon or krypton.

In a modification of the steps described above, a resin may be included in the mixture before heating, and most of the resin is then removed by heating in a vacuum leaving some residual resin, for example 2% by weight, in the finished magnetic material.

Figure 2 is a chart of the magnetic properties of materials made from the above constituents by the above method, the differences between the materials arising from the different proportions of the various constitu-

ents and Figures 3c to 3f give further details.

Figure 4 is a short comparing the properties of the magnetic materials in accordance with the invention (sintered Nd-Fe-B) with the magnetic materials described in the later Croat specification (bonded Nd-Fe-B) and with traditional magnetic materials ($SmCo^5$ and Sm^2Co^{17}).

Claims

1. A method of making a material with permanent magnetic properties at room temperature comprising the steps of :-
   (a) forming a mixture of iron, neodymium and other elements;
   (b) heating the mixture;
   (c) cooling the mixture;
   characterized in that :-
   (d) the elements are ground into a powder so that the mixture is formed of particles of size less than 10 microns;
   (e) the mixture comprises by atomic weight per cent approximately
   not more than 50% neodymium (Nd)
   not more than 4% cobalt (Co)
   not more than 20% dysprosium (Dy)
   not more than 15% boron (B)
   not more than 12% molybdenum (Mo)
   not more than 15% niobium (Nb)
   (f) the mixture is pressed into the desired finished shape before heating;
   (g) the preparation of the particles, the mixing and the pressing are carried out in a lower oxygen moisture free environment;
   (h) heating is effected so that the temperature rises in a series of cycles each comprising a period of sharply increasing temperature followed by substantially constant temperature;
   (i) heating continues until the mixture reaches sintering temperature; and
   (j) The mixture cools slowly.

2. A material with permanent magnetic properties made by the above method.

Patentansprüche

1. Verfahren zur Herstellung eines Materials mit Permanentmagneteigenschaften bei Raumtemperatur, bei dem
   (a) eine Mischung aus Eisen, Neodym und andern Elementen gebildet wird,
   (b) die Mischung erhitzt wird,
   (c) die Mischung abgekühlt wird,
   dadurch gekennzeichnet, daß
   (d) die Elemente zu Pulver vermahlen werden, so daß die Mischung aus Teilchen mit einer Größe von weniger als 10 µm gebildet wird;
   (e) die Mischung (in Atom-Gew.%) ungefähr
   nicht mehr als 50 % Neodym (Nd)
   nicht mehr als 4 % Kobalt (Co),
   nicht mehr als 20 % Dysprosium (Dy),
   nicht mehr als 15 % Bor (B),
   nicht mehr als 12 % Molybdän (Mo),
   nicht mehr als 15 % Niob (Nb) umfaßt,
   (f) die Mischung vor dem Erhitzen in die gewünschte fertige Gestalt gepresst wird,
   (g) die Herstellung der Teilchen, das Mischen und das Pressen in einer feuchtigkeitsfreien Umgebung mit niedrigem Sauerstoffgehalt durchgeführt wird,
   (h) das Erhitzen bewirkt wird, so daß die Temperatur in einer Reihe von Cyclen steigt, von denen jeder einen Zeitraum von scharf ansteigender Temperatur gefolgt von im wesentlichen konstanter Temperatur umfaßt,
   (i) das Erhitzen fortgesetzt wird, bis die Mischung Sintertemperatur erreicht und

(j) die Mischung langsam abkühlt.

2. Material mit Permanentmagneteigenschaften, das nach dem obigen Verfahren hergestellt ist.

Revendications

1. Procédé d'élaboration d'un matériau à propriétés magnétiques permanentes à la température ambiante, comprenant les opérations consistant:
   (a) à former un mélange de fer, de néodyme et d'autres éléments,
   (b) à chauffer le mélange et
   (c) à refroidir le mélange,
   caractérisé en ce que :
   (d) on broie les éléments de façon à former une poudre, d'une manière telle que le mélange soit formé de particules ayant une taille inférieure à 10 micromètres,
   (e) le mélange comprend approximativement, en pourcentage en poids atomique :
   pas plus de 50 % de néodyme (Nd),
   pas plus de 4 % de cobalt (Co),
   pas plus de 20 % de dysprosium (Dy),
   pas plus de 15 % de bore (B),
   pas plus de 12 % de molybdène (Mo) et
   pas plus de 15 % de niobium (Nb),
   (f) on comprime le mélange, avant chauffage, sous la forme finale voulue,
   (g) on exécute la préparation des particules, le mélange et la compression dans un milieu environnant dépourvu d'humidité et à faible teneur en oxygène,
   (h) on procède au chauffage d'une façon telle que la température s'élève suivant une série de cycles comprenant chacun une période d'augmentation rapide de la température suivie d'une période à température pratiquement constante,
   (i) on poursuit le chauffage jusqu'à ce que le mélange atteigne la température de frittage et
   (j) le mélange se refroidit lentement.

2. Matériau à propriétés magnétiques permanentes élaboré par le procédé ci-dessus.

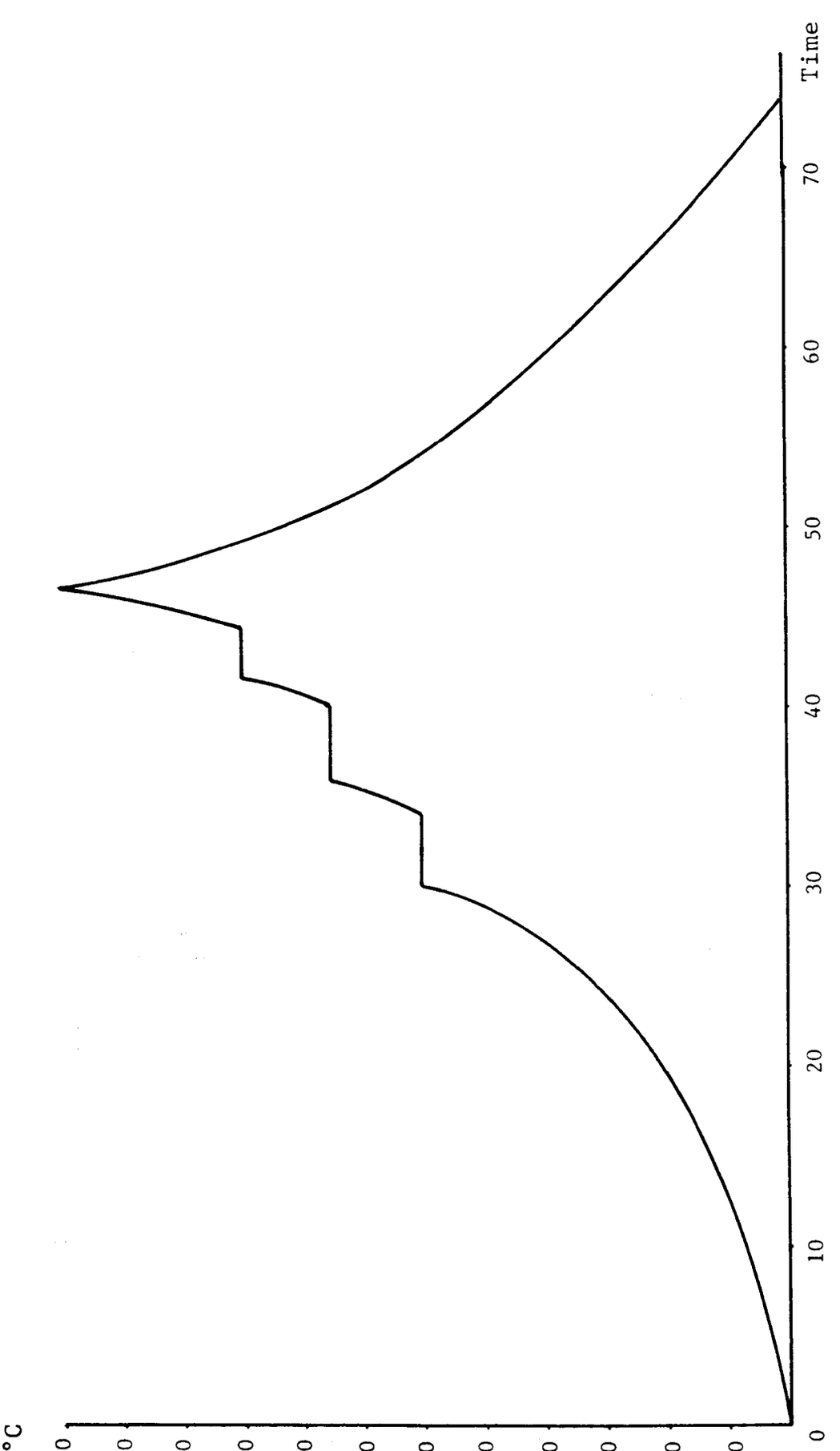

°C
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
10
20
30
40
50
60
70
Time

FIG. 1

TYPE	RESIDUAL FLUX DENSITY Br (KG)	COERCIVE FORCE bHc (KOe)	INTRINSIC COERCIVE FORCE iHc Nom. (KOe)	MAXIMUM ENERGY PRODUCT (BH) Max. (MGOe)	AVERAGE TEMPERATURE Br (-%/C°)	AVERAGE TEMPERATURE iHc (-%/C°)	DENSITY d (g/cm^3)	RECOIL PERMEABILITY μ rec	VICKERS HARDNESS Hv	MAXIMUM TEMPERATUE @ INTRINSI COERCIVE FORCE iHc
N-27	10.2-11.0	9-10.5	14	25 - 28	0.12	0.6	7.3-7.4	1.05	500-600	100°C
N-30	10.8-11.5	9.5-10.5	14	28 - 31	0.12	0.6	7.3-7.5	1.05	500-600	100°C
N-33	11.3-11.7	10-11.1	14	31 - 33	0.12	0.6	7.4-7.5	1.05	500-600	100°C
N-35	11.8-12.2	11.0-11.7	14	33 - 36	0.12	0.6	7.4-7.5	1.05	500-600	100°C
27-H	10.2-11.0	9.6-10.5	17	25 - 28	0.11	0.58	7.4-7.5	1.05	500-600	120°C
30-H	10.8-11.5	10.2-10.7	17	28 - 31	0.11	0.58	7.4-7.5	1.05	500-600	120°C
33-H	11.3-11.7	10.6-11.1	17	31 - 33	0.11	0.58	7.4-7.5	1.05	500-600	120°C
35-H	11.8-12.2	11.0-11.7	17	33 - 36	0.11	0.55	7.4-7.5	1.05	500-600	120°C
27SH	10.2-11.0	9.6-10.5	20	25 - 28	0.11	0.55	7.4-7.5	1.05	500-600	150°C
30SH	10.8-11.5	10.2-10.7	20	28 - 31	0.11	0.55	7.4-7.5	1.05	500-600	150°C

FIG. 2

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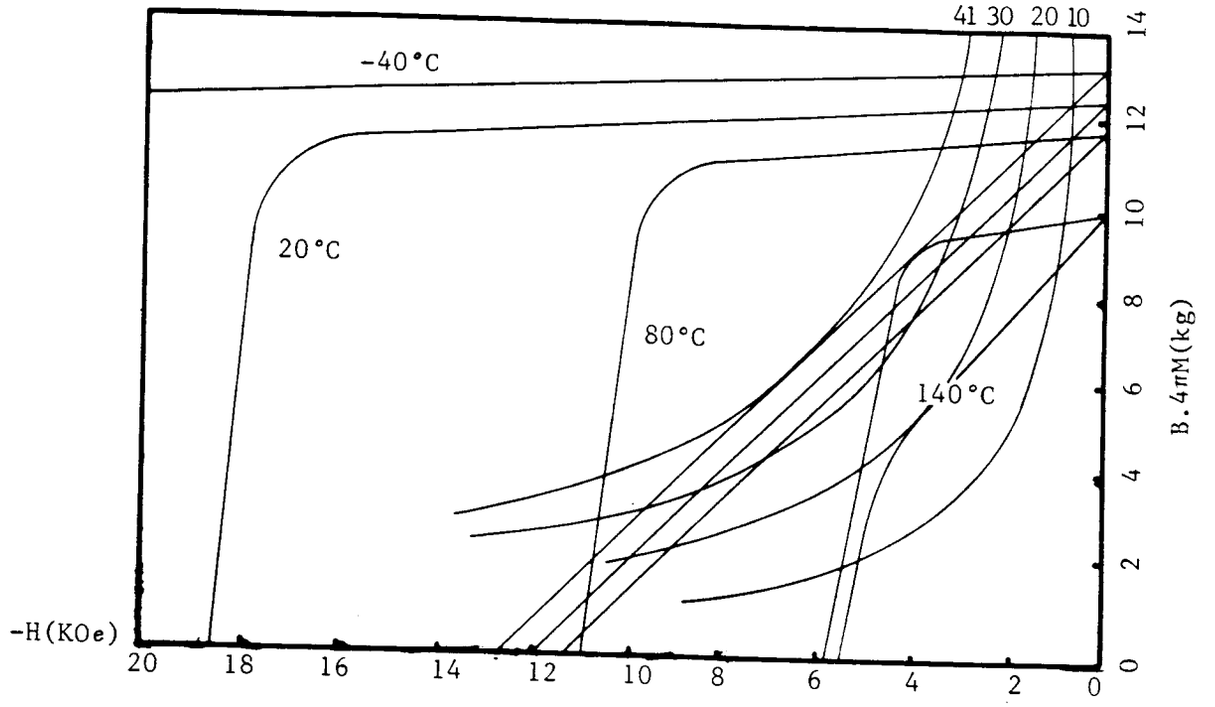

41 30 20 10
-40°C
20°C
80°C
140°C
-H(KOe)
20 18 16 14 12 10 8 6 4 2 0
0 2 4 6 8 10 12 14
B.4πM(kg)

FIG. 3a

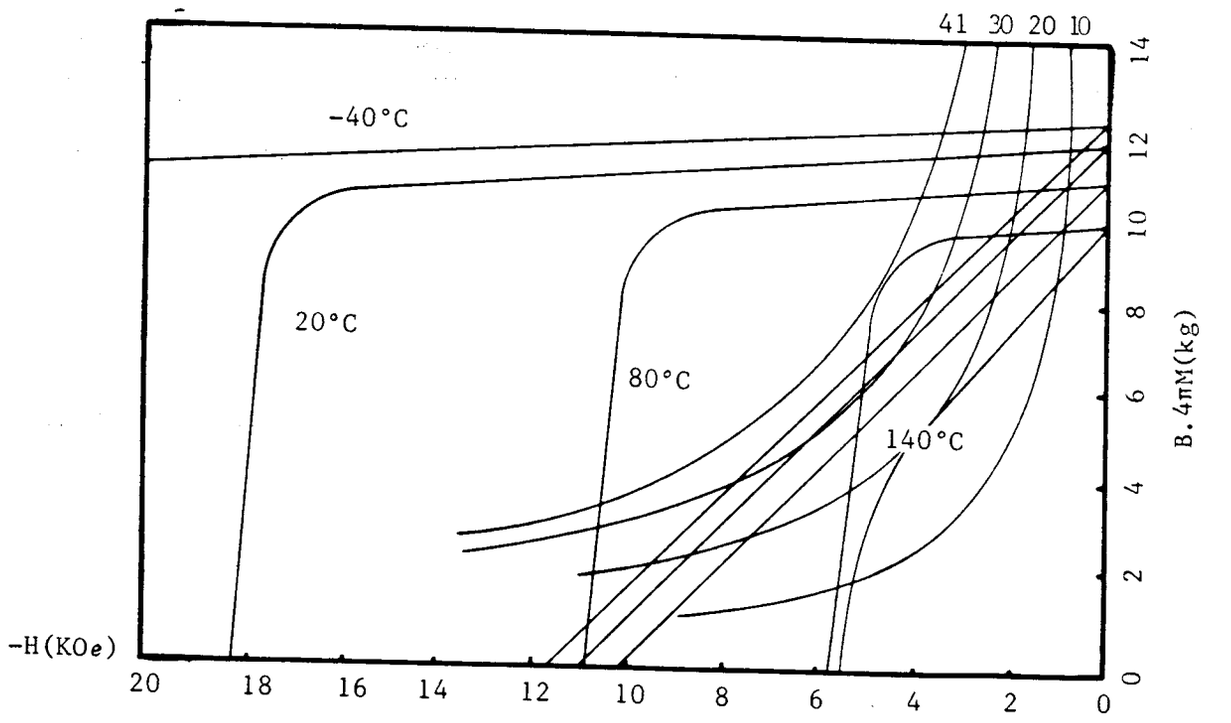

41 30 20 10
-40°C
20°C
80°C
140°C
-H(KOe)
20 18 16 14 12 10 8 6 4 2 0
0 2 4 6 8 10 12 14
B.4πM(kg)

FIG. 3b

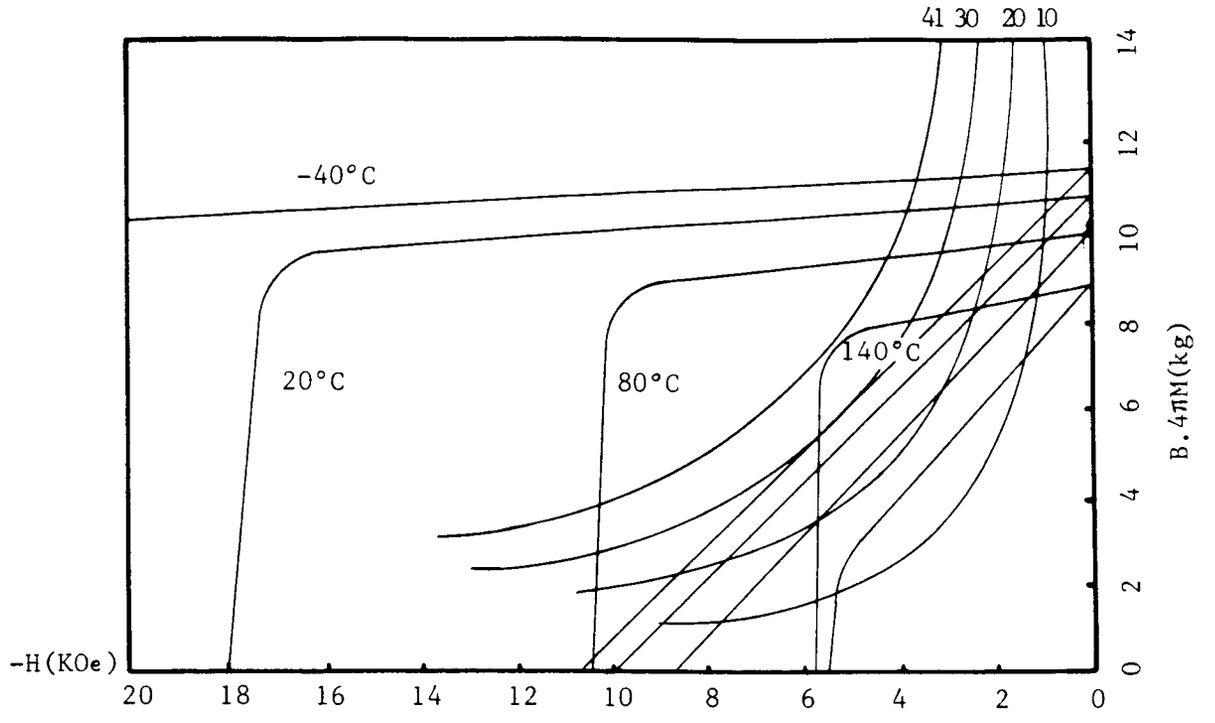

41 30 20 10
-40°C
20°C
80°C
140°C
-H(KOe)
20 18 16 14 12 10 8 6 4 2 0
0 2 4 6 8 10 12 14
B.4πM(kg)

FIG. 3c

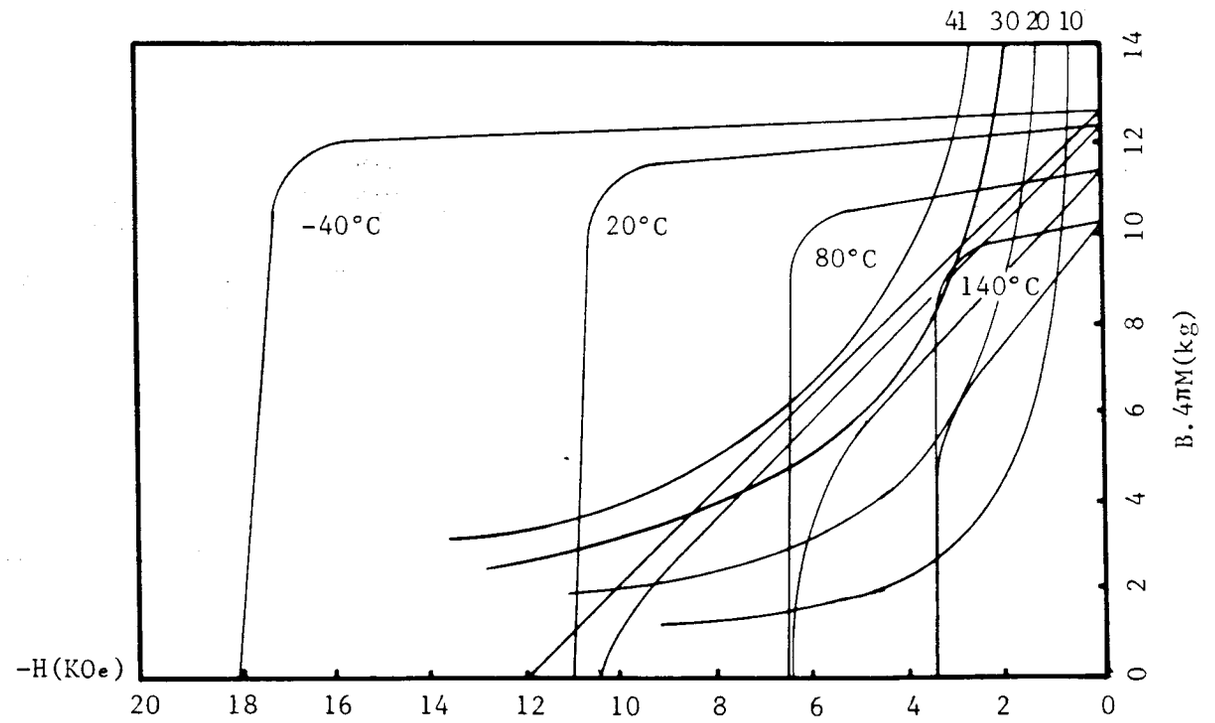

41 30 20 10
-40°C
20°C
80°C
140°C
-H(KOe)
20 18 16 14 12 10 8 6 4 2 0
0 2 4 6 8 10 12 14
B.4πM(kg)

FIG. 3d

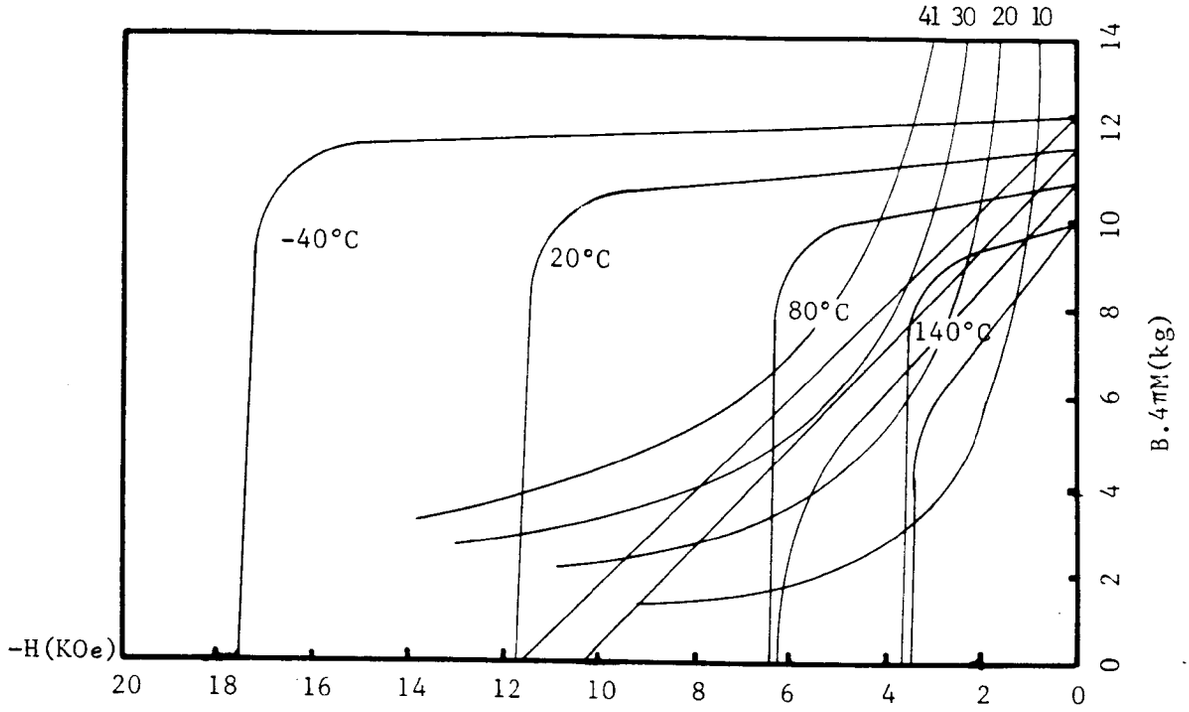

41 30 20 10
-40°C
20°C
80°C
140°C
-H(KOe)
20 18 16 14 12 10 8 6 4 2 0
0 2 4 6 8 10 12 14
B.4πM(kg)

FIG. 3e

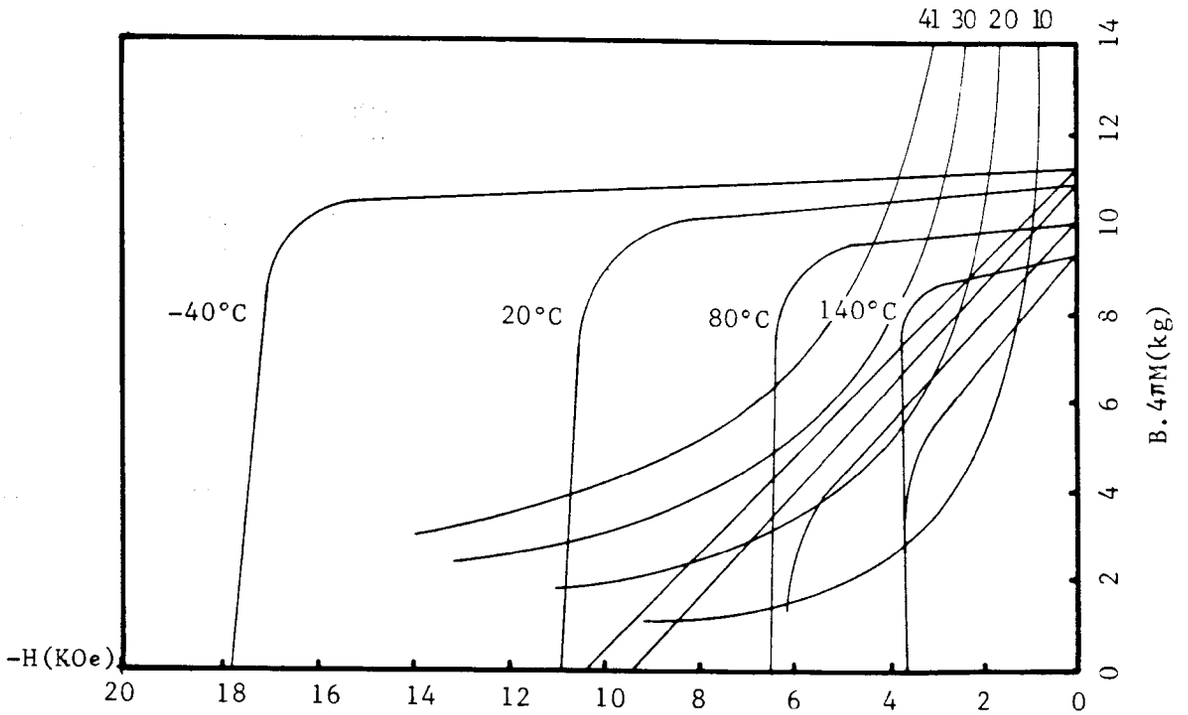

41 30 20 10
-40°C
20°C
80°C
140°C
-H(KOe)
20 18 16 14 12 10 8 6 4 2 0
0 2 4 6 8 10 12 14
B.4πM(kg)

FIG. 3f

TYPE	RESIDUAL FLUX DENSITY Br (KG)	COERCIVE FORCE bHc (KOe)	INTRINSIC COERCIVE FORCE iHc Nom. (KOe)	MAXIMUM ENERGY PRODUCT (BH)Max. (MGOe)	DENSITY D (g/cm^3)	RECOIL PERMEA-BILITY u rec	VICKERS HARDNESS Hv	AVERAGE TEMPERATURE Br (-%/C°)	AVERAGE TEMPERATURE iHc (-%/C°)	CURIE TEMPER-ATURE Tc °C	MAXIMUM TEMPERATURE @INTRINSIC COERCIVE FORCE. iHc
$SmCo_5$,											
" 18,	8.0-8.8	7.5-8.5	15	16-19	8.2-8.4			0.045	0.2-0.3	720	
" 20,	8.5-9.5	8.0-9.5	15	18-21	8.2-8.4			0.045	0.2-0.3	720	
" 22,	9.0-10.0	8.5-10.0	10	20-24	8.2-8.4			0.050	0.2-0.3	700	
Sm_2Co_{17},											
" 21,	9.4-10.4	5.0-8.0	5.3	19-23	8.2-8.4			0.035	0.2-0.3	820	
" 23,	9.5-10.5	5.0-8.0	5.3	21-25	8.2-8.4			0.035	0.2-0.3	820	
" 24,	9.8-10.8	8.0-10.0	10	22-26	8.2-8.4			0.035	0.2-0.3	820	
" 26,	10.2-11	8.5-10.5	10	24-28	8.2-8.4			0.035	0.2-0.3	820	
BONDED Nd-Fe-B											
" A8	6.4-7.2	4.5-5.5	7-10	8-10	5.6-6.2			0.090	0.35-0.56		
" B7	5.6-6.5	5.0-5.5	13-15	7-9	5.6-6.2			0.120	0.35-0.56		
SIN-TERED Nd-Fe-B											
" N30,	10.8-11.5	9.5-10.5	14	28-31	7.3-7.5	1.05	500-600	0.12	0.6	300-330	100°C
" N35,	11.8-12.2	9.5-10.5	14	33-36	7.4-7.5	1.05	500-600	0.12	0.6	300-330	100°C
" 30H,	10.8-11.5	10.2-10.7	17	28-31	7.4-7.5	1.05	500-600	0.11	0.58	300-330	120°C
" 35H,	11.8-12.2	11.0-11.7	17	33-36	7.4-7.5	1.05	500-600	0.11	0.55	300-330	120°C

FIG. 4

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