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(54) **Sm₂Co₁₇ alloys suitable for use as permanent magnets.**

(57) An Sm₂Co₁₇ alloy is disclosed suitable for use as a permanent magnet having a high energy product and a high intrinsic coercivity and containing 22.5 to 23.5% by weight Sm as a first amount, 20.0 to 25.0% by weight Fe, 3.0 to 5.0% by weight Cu, a first amount of Zr in the range 1.4 to 2.0% by weight, a minor amount of oxygen and a minor amount of carbon, an additional amount of Sm in the range of from 4 to 9 times the oxygen content of the alloy, an additional amount of Zr in the range of from 5 to 10 times the carbon content of the alloy, and the balance being cobalt, the alloy having a crystallographic structure comprising cells of 2-17 Sm-Co rhombohedral phase surrounded by a continuous network of the 1-5 Sm-Co hexagonal phase. Part of the Sm can be replaced by Pr and all or part of the Zr can be replaced by a different Group IVB or VB metal e.g. Hf.

Sm₂Co₁₇ ALLOYS SUITABLE FOR USE
AS PERMANENT MAGNETS

This invention relates to Sm₂Co₁₇ alloys suitable for use as permanent magnets.

The advantages of rare earth cobalt alloy magnets are now well known. Such magnets are specially
5 suitable for use in electric motors, such as DC servomotors. It is also known that Sm₂Co₁₇ alloys have potential advantages for use as permanent magnets over SmCo₅ alloys(1). For example, DC motors using Sm₂Co₁₇ alloy magnets have lower weight and inertia and
10 increased torque and acceleration compared to the use of SmCo₅ alloy magnets.

Various attempts have been made to provide Sm₂Co₁₇ alloys which can form permanent magnets having a high energy product (BH)_{max} and a high intrinsic
15 coercivity iH_c. Typical prior art is shown for example in United States patent No. 4,172,717 issued October 30, 1979 to Tokunaga et al(2), United States patent No. 4,213,803 issued July 22, 1980 to Yoneyama et al(3), United States patent No. 4,221,613 issued September 9,
20 1980 to Imaizumi et al(4) and United States patent No. 4,375,996 issued March 8, 1983 to Tawara et al(5). Other prior art is shown in the published literature(6,7,8,9,10).

As disclosed in the above-mentioned prior art, $\text{Sm}_2\text{Co}_{17}$ alloys are known which can form magnets having an energy product $(\text{BH})_{\text{max}}$ in the range of 22 to 30 MGOe and an intrinsic coercivity iH_c in the range of 5.8 to 6.3 kOe(6,7). Later developments have resulted in the production of $\text{Sm}_2\text{Co}_{17}$ alloys which can produce magnets with higher coercivity, but this advantage has been offset by loss in energy product. For example, one $\text{Sm}_2\text{Co}_{17}$ alloy is now known which can produce magnets having an energy product $(\text{BH})_{\text{max}}$ of 26 MGOe and an intrinsic coercivity iH_c of 15.0 kOe(7). Another $\text{Sm}_2\text{Co}_{17}$ alloy now known has an energy product $(\text{BH})_{\text{max}}$ of 27 MGOe and an intrinsic coercivity iH_c of 10.0 kOe, see United States patent No. 4,375,996 mentioned above(5).

It is also known that, because of different magnetic hardening mechanisms, $\text{Sm}_2\text{Co}_{17}$ alloys are harder to magnetize from an unmagnetized state than SmCo_5 alloys. For example, in the construction of electric motors, it is the preferred practice to construct the field or stator assembly with unmagnetized magnets, and then magnetize the finished assembly as a single unit. This preferred industrial practice imposes an upper limit of about 25 kOe on the intensity of the magnetizing field which can be applied to the unmagnetized magnets of a typical assembly. Thus, in order to be useful in practice, an unmagnetized magnet must be capable of attaining its specified properties in a magnetizing field of 25 kOe. To date, it has not been possible to achieve this requirement with $\text{Sm}_2\text{Co}_{17}$ alloys with an energy product greater than 30 MGOe(6).

Thus, although it is acknowledged that $\text{Sm}_2\text{Co}_{17}$ alloys have potential advantages over other rare earth/transition metal alloys such as SmCo_5 alloys, $\text{Sm}_2\text{Co}_{17}$ alloys have not yet become practically useful because improved coercivity has only been obtainable at

the expense of energy product and also because such alloys have not been capable of attaining their specified properties in a magnetizing field up to about 25 kOe.

5 It is therefore an object of the invention to provide an $\text{Sm}_2\text{Co}_{17}$ alloy which overcomes these disadvantages.

 According to the present invention, an $\text{Sm}_2\text{Co}_{17}$ alloy contains by weight:

10 22.5 to 23.5% Sm as an effective amount,
 20.0 to 25.0% Fe,
 3.0 to 5.0% Cu,
 1.4 to 2.0% Zr as an effective amount.

 Further, in order to compensate for minor
15 amounts of oxygen and carbon which are inevitably present in practice, it has been found that an additional amount of Sm should be provided to compensate for the oxygen content and that an additional amount of Zr should be provided to compensate for the carbon content. Thus, an
20 alloy in accordance with the invention also includes an additional amount of Sm in the range of from about 4 to about 9 times the oxygen content of the alloy, preferably 6.265 times the oxygen content, and an additional amount of Zr in the range of from about 5 to about 10 times the
25 carbon content of the alloy, preferably 7.595 times the carbon content. The remainder of the alloy content is cobalt.

 The function of the "effective samarium" is to develop the desired crystallographic structure consisting
30 of cells of the 2-17 Sm-Co rhombohedral phase surrounded by a continuous network of the 1-5 Sm-Co hexagonal phase(11,12,13). It is necessary that the 1-5 network be continuous to develop the desired second quadrant loop squareness, that is to say a maximum value of H_K , and
35 this is dependent upon the "effective samarium" present. Sufficient samarium must be present for this purpose but

too much samarium results in the breakdown of the 2-17 rhombohedral phase and loss of remanent induction B_r . The function of the "effective samarium" present is therefore to develop the 2-17 Sm-Co rhombohedral phase having high remanent induction B_r and to develop a complete 1-5 Sm-Co hexagonal phase network to develop the coercivity or magnetic hardening. Too little samarium results in an incomplete 1-5 Sm-Co network and incomplete hardening, that is to say a low H_K , and too much samarium results in breakdown of the 2-17 Sm-Co phase and loss of remanent induction B_r and energy product $(BH)_{max}$. Precise control of the "effective samarium" content is necessary to obtain optimum properties and this can be achieved by the present invention.

The function of the "effective zirconium" is to facilitate the dissolution of all the desired constituents into one single phase solid solution in the solution heat treatment stage of the processing. Only when this is achieved is it possible to establish complete homogeneity as the necessary starting point to develop in the subsequent aging heat treatment the desired structure consisting of 2-17 Sm-Co cells surrounded by a continuous network of the 1-5 Sm-Co boundary phase. The presence of zirconium distorts the Sm-Co lattice so as to reduce the c/a ratio of the hexagonal unit cell⁽¹⁴⁾ and this facilitates the accommodation of the desired elements in single phase solid solution during the solution heat treatment at 1140-1170°C. At elevated temperatures the 2-17 Sm-Co composition has a hexagonal crystal lattice but at room temperature it transforms to a rhombohedral crystal lattice. These two crystal systems are closely related and the rhombohedral lattice can be regarded as an imperfect hexagonal lattice containing stacking faults. The desired equilibrium structure at room temperature consists of cells of the 2-17 Sm-Co rhombohedral phase

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surrounded by a continuous network of the 1-5 Sm-Co hexagonal phase. It has also been observed that for a fixed copper content the coercivity increases with the zirconium content. Thus to achieve the objective of easier magnetization it is necessary to keep the zirconium content to a minimum commensurate with the above stated requirements regarding the single phase solid solution. The necessary precise control of the "effective zirconium" content can be achieved by the present invention.

By using an $\text{Sm}_2\text{Co}_{17}$ alloy in accordance with the invention, it is possible to produce a permanent magnet which attains its specified properties in a magnetizing field of about 25 kOe, has an energy product $(\text{BH})_{\text{max}}$ of at least 30 MGOe and has a satisfactory coercivity iH_c of 14-16 kOe. A magnet in accordance with the present invention can also have a satisfactory remanent induction B_r of at least about 11.5 kG, and a better loop squareness in the second quadrant, i.e. H_K of approximately 9.0 kOe.

Preferably, the oxygen content of the alloy is not greater than about 0.6% by weight, and the carbon content of the alloy is not greater than about 0.1% by weight.

Also, the alloy preferably contains:
23.0% Sm as an effective amount,
22.0% Fe,
4.6% Cu,
1.5% Zr as an effective amount,
minor amounts of oxygen and carbon,
additional amounts of Sm and Zr as specified above.
and the balance being cobalt.

The invention is at least partly based upon the realization that it is possible to compensate for small

traces of carbon present in many of the elements that are used in the production of the alloy and which have an adverse effect on the magnetic properties of the alloy. In accordance with the invention, compensation is made
 5 for the carbon content by providing an additional amount of zirconium as specified above.

The additional zirconium may be incorporated in the alloy by adding zirconium in the form of a master alloy to an $\text{Sm}_2\text{Co}_{17}$ base alloy at a convenient stage in
 10 the processing, for example prior to compacting and sintering the alloy powder. The master alloy may be of a simple form such as ferrozirconium, which is a low melting point (about 935°C) eutectic containing 83% Zr and 17% Fe by weight. Ferrozirconium may be successfully
 15 used when only a small additional amount of zirconium is required. In other words, only up to about 2% ferrozirconium by weight should be added.

If a larger additional amount of zirconium has to be added, it is preferable to utilize a master alloy
 20 with the same composition as the base alloy with the exception that the master alloy should contain a larger amount of zirconium, for example from about 5 to 10% by weight, the increase in the zirconium content being achieved at the expense of the cobalt content.

25 The following table illustrates the compensation of zirconium content for carbon present and the optimum zirconium level at about 1.5%.

30	Total Zr (%)	C (%)	Cx6.265 (%)	Effective Zr (%)	B_r (kG)	iH_c (kOe)	H_K (kOe)
	2.24	0.07	0.53	1.71	11.6	19.1	8.3
	2.1	0.072	0.55	1.55	11.7	16.9	9.8
	2.05	0.068	0.52	1.53	11.6	15.2	8.9
35	2.0	0.195	1.48	0.52	1.6	0.2	0.1

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The present invention is also at least partly based on the realization that it is possible to compensate for the small traces of oxygen which are picked up by the alloy during its manufacture and which have an adverse effect on the magnetic properties of the alloy. In accordance with the invention, the small traces of oxygen are compensated for by addition of an additional amount of samarium as specified above. The amount of oxygen in the final product can be estimated from the oxygen content of the starting material or more preferably determined by analyzing a sample product.

The samarium addition may be accomplished by adding a samarium rich alloy to a $\text{Sm}_2\text{Co}_{17}$ base alloy at a convenient stage in the processing, for example prior to compacting and sintering the alloy powder. It is not practicable to add elemental samarium because of its high rate of oxidation. The samarium rich alloy preferably has the same composition as the base alloy except that the samarium content would be about 1 to 3% higher than in the base alloy, the higher samarium content being achieved at the expense of the cobalt content. A simple binary master alloy (such as 60% Sm, 40% Co) can also be used to add Sm.

The following table illustrates the compensation of samarium content for oxygen present and the optimum effective samarium in the range 22.5-23.5%.

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	Total Sm (%)	O ₂ (%)	O ₂ x6.265 (%)	Effective Sm (%)	B _r (kG)	iH _c (kOe)	H _k (kOe)
5	24.6	0.44	2.76	21.8	9.62	4.0	1.85
	25.1	0.42	2.63	22.5	11.64	19.45	6.25
	25.3	0.42	2.63	22.7	11.73	17.9	9.1
	26.0	0.55	3.45	22.6	11.65	16.9	9.8
	26.1	0.56	3.51	22.6	11.54	17.7	8.9
10	26.0	0.38	2.38	23.6	11.3	15.9	6.3

By adding additional zirconium and samarium to compensate for the inevitable presence of small traces of carbon and oxygen in the alloy, it has been found to be possible to define more precisely the alloy composition in order to produce the preferred magnetic properties.

Thus, the preferred samarium range is 22.5 to 23.5% with the preferred samarium value being 23.0% Sm. This is the effective amount, as compared to the additional amount provided as specified to compensate for oxygen content. The range of effective samarium content is considerably narrower than has been specified in the prior art.

The effective zirconium range has been specified to be from 1.4 to 2.0% with the preferred value being 1.5%. Thus, with the present invention, it has been possible to specify a zirconium range which is considerably narrower than that taught by the prior art.

It has also been found possible to optimize the iron and copper contents. The composition limits of iron, copper and zirconium are interrelated and each can critically affect the existence of the single phase structure. It is known that the addition of iron to the 2-17 Sm-Co system increases the remanent induction

provided that the structure can be maintained as a single 2-17 Sm-Co phase. If the optimum iron content is exceeded the alloy breaks down into an Fe-rich eutectoid structure having lower remanent induction. It has been
5 observed that the copper content acts to increase the coercivity or magnetic hardness of the alloy. It is believed that copper concentrates in the 1-5 Sm-Co phase network and enhances the coherent nucleation of regions of 2-17 Sm-Co phase within the 1-5 Sm-Co phase network
10 during cooling from the aging temperature, thereby creating lattice strain and magnetic hardness or coercivity(15).

The iron content has been specified to be 20.0 to 25.0%, preferably 22.0%, and the copper content has
15 been specified to be 3.0 to 5.0%, preferably 4.6%. The iron content has also been defined within a much narrower range than has been taught by the prior art. Similar remarks apply to the copper content. As previously indicated, cobalt forms the balance of the composition.

20 An $\text{Sm}_2\text{Co}_{17}$ alloy in accordance with the invention is preferably made in the following manner. The alloy of the desired composition was produced by pulverizing melted and cast alloy into particles of 3-8 μ m size. Small additions of ferrozirconium and a samarium
25 rich alloy of similar composition to the parent alloy were then blended in to compensate for the deleterious effects of the trace amounts of carbon and oxygen present according to the present invention. The blended powders were aligned in a die under a transverse magnetic field
30 of 12 kOe and compacted under a pressure of 60 kpsi. The green compact was sintered in hydrogen at 1150°C for 30 min. The atmosphere was then changed to argon and the compact was heated to 1205°C at a rate of 4-5°C/min, held at 1205°C for 10 min and then cooled to 1160°C at
35 2°C/min. The sample was then solution treated at

1140-1160°C for 2 hours, quenched from 1140-800°C at 10°C/s and air cooled from 800°C to room temperature. It was then reheated to 845±5°C and held for 20 hours, cooled at about 2°C/min from 845°C to about 600°C and at about 1°C/min from about 600°C to 410°C, held at 410°C for 10 hours and cooled to room temperature.

An $\text{Sm}_2\text{Co}_{17}$ alloy having the previously mentioned preferred composition in accordance with the invention and produced in the above described manner achieved the following properties:

$(BH)_{\text{max}}$	B_r	iH_c	H_c	H_K
<u>MGOe</u>	<u>kG</u>	<u>kOe</u>	<u>kOe</u>	<u>kOe</u>
30.8	11.7	15.8	11.0	9.0

The advantage of the invention can readily be seen from the above Table.

It has also been found that praseodymium can be substituted in part for samarium in the alloy of the present invention without decreasing the aforementioned desirable properties. To preserve the required 2-17 Sm-Co rhombohedral crystal structure the substitution of praseodymium must be made on an atomic basis, that is to say since praseodymium has a lower atomic weight than samarium, on a weight percent basis less praseodymium will be required in the alloy than the weight percent of samarium replaced. In the example illustrated below it was found that whereas optimum properties were obtained with 23.0% effective samarium in the standard alloy, when a combination of samarium and praseodymium was used the optimum properties were obtained with an effective amount of 22.5% (Sm + Pr), comprising 20.0% Sm + 2.5% Pr. Furthermore, in calculating the effective amount of praseodymium present with respect to that amount which has been rendered ineffective by combination with oxygen, account must be taken of the molecular weight of the praseodymium oxide and the correction factor of 6.265

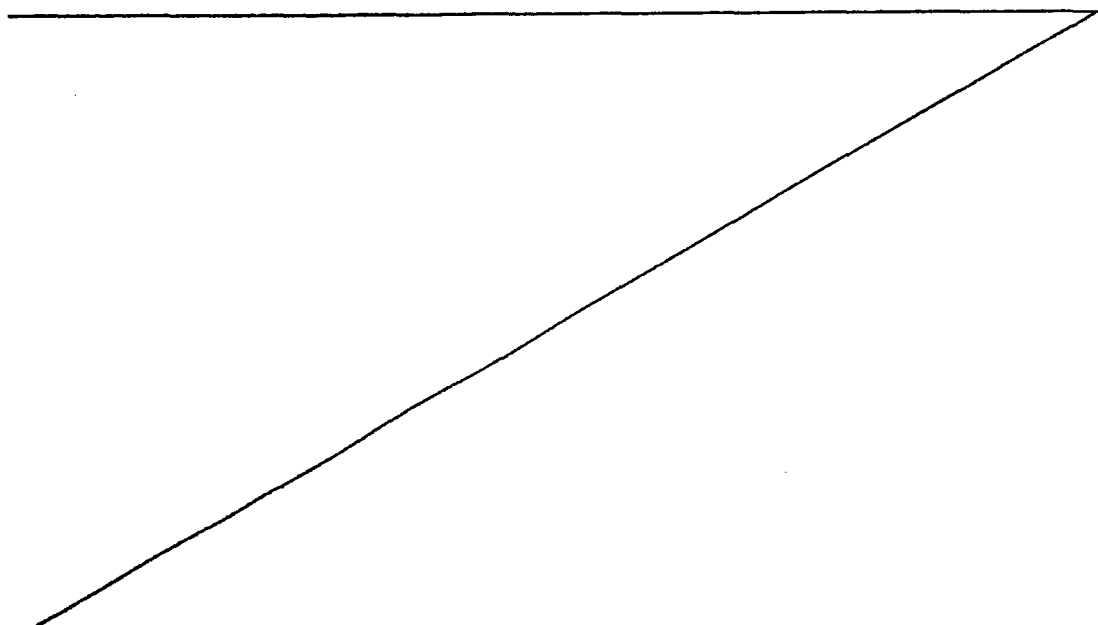
times the oxygen content for samarium must be changed to 5.871 for the praseodymium added. Also, as is described more fully in a copending European Application filed simultaneously herewith and claiming priority from U.K. 8403751 and to which reference should be made, in the production of high strength 2-17 Sm-Co permanent magnets from the alloys of the present composition the selection of a solution treatment temperature which is marginally below the liquid plus solid phase transformation temperature for the specific alloy composition is important. In the case where praseodymium has been partially substituted for samarium care must be taken since the liquid plus solid phase transformation temperature will be lower than that of the standard samarium alloy by an amount depending on the level of praseodymium substituted. The following example illustrates the partial replacement of samarium by praseodymium. An alloy containing 20.3% Sm and 2.17% Pr as effective amounts was prepared as described earlier with the exception that the solution treatment step was carried out in the range 1130-1150°C. The following properties were obtained and are compared with those of a similar alloy containing only samarium as the rare earth element.

Eff. Sm (%)	Eff. Pr (%)	Fe (%)	Cu (%)	Zr (%)	Co (%)	B _r (kG)	jH _c (kOe)	H _K (kOe)
20.3	2.17	20.5	5.2	2.5	bal	11.6	22.65	8.7
23.8	-	20.5	5.2	2.5	bal	11.5	22.4	9.7

It has also been found that other group IVB or VB transition elements may be substituted full or in part for zirconium in the alloy of the present invention. Since the function of the group IVB or VB transition element is to reduce the c/a ratio of the 2-17 Sm-Co hexagonal unit cell, the replacement of zirconium by other elements must

be made on an atomic basis. Furthermore in calculating the effective amount of the transition metal present with respect to that amount rendered ineffective by combination with carbon, account must be taken of the molecular weight of the transition metal carbide and the correction factor of 7.595 times the carbon content of the alloy must be adjusted accordingly. For example, in the case of hafnium the correction factor would be 14.862 times the carbon content of the alloy. Moreover, and as is pointed out in said copending application, in the process for the production of high strength 2-17 Sm-Co permanent magnets from these alloys, the aging temperature is critically dependent upon the zirconium content. Thus where other group IVB or VB transition elements are substituted for zirconium in the alloy the optimum aging temperature and time may be different from those referred to above where Zr is the sole group IVB or VB element. The following example illustrates the substitution of hafnium for zirconium in an alloy of the present invention. An alloy was prepared as described earlier for the standard alloy except that zirconium as an effective amount was replaced by hafnium as an effective amount. In calculating the additional amount of hafnium required to arrive at the effective amount the carbon content of the alloy was multiplied by the factor 14.862. The alloy was processed as described earlier for the standard alloy with the exception that after quenching from the solution temperature to room temperature the alloy was reheated to an aging temperature of $845 \pm 5^{\circ}\text{C}$ and held there for 24 hours.

The following table illustrates the replacement of zirconium by hafnium as an effective amount.



5

Total Zr (%)	C (%)	Cx7.595 (%)	Effective Zr (%)	$B_r^{(1)}$ (kG)
1.78	0.07	0.53	1.25	10.6
1.90	0.07	0.53	1.37	10.9

10

Total Hf (%)	C (%)	Cx14.862 (%)	Effective Hf (%)	$B_r^{(1)}$ (kG)
3.65	0.082	1.22	2.43	10.6
3.80	0.082	1.22	2.58	10.7

15

(1) The results in the above table are for parallel aligned magnets. The residual induction (B_r) for the same magnets transversely aligned would be approximately 1.0 kG higher, i.e. 11.6-11.9 kG.

20 The invention thus also provides an $\text{Sm}_2\text{Co}_{17}$ alloy permanent magnet containing also iron, copper and zirconium or similar group IVB or VB transition metals, said alloy containing: an effective amount of samarium, in addition to that samarium combined with oxygen, such

25 that after the aging stage of the process the crystal structure of the alloy consists of the single phase 2-17 Sm-Co rhombohedral structure containing a continuous network of the 1-5 Sm-Co phase, an effective amount of zirconium, in addition to that zirconium combined with

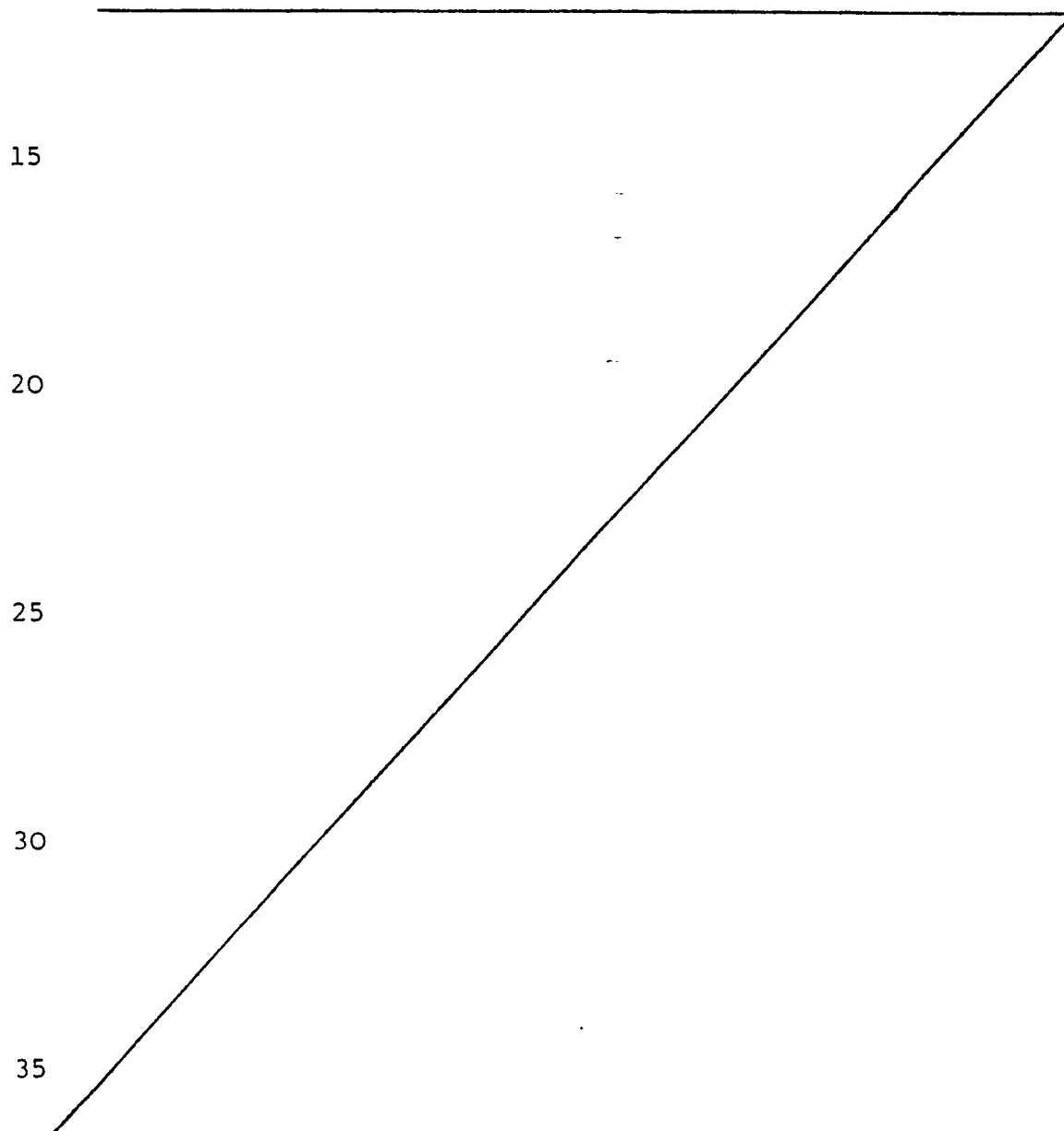
30 carbon, such that during the solution heat treatment stage of the process the 2-17 Sm-Co crystal lattice is distorted to facilitate the dissolution of all the constituents of said alloy into a uniform single phase solid solution, an amount of iron being as high as possible to

35 maximize the remanent induction of said alloy whilst

still maintaining the single phase 2-17 Sm-Co uniform solid solution in the solution heat treatment stage of the process, an amount of copper such that during the cooling stage from the aging temperature the coherent
5 nucleation of 2-17 Sm-Co phase within the 1-5 Sm-Co phase network is enhanced to produce lattice strain and coercivity, it being understood that both zirconium and copper levels must be controlled to permit the iron level to be optimized whilst still maintaining a uniform solid solution in the solution heat treatment stage.

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The optimization of composition must be based on the requirement that all the alloying elements are first put into a uniform solid solution. In the studies of composition variations in Fe, Cu and Zr it was found that the optimum effective samarium content remained constant at $23 \pm 0.5\%$. However, it was found that the effective samarium content can be partly replaced by praseodymium with the added observation that slightly less (Sm+Pr) is required for optimum properties. From an economic point of view this could be an attractive alternative.

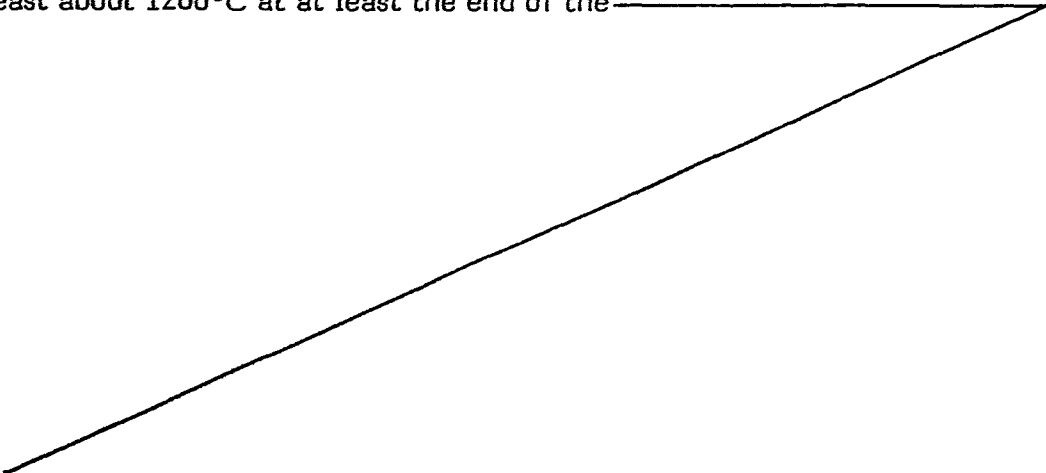


In more detail the alloys described above can be produced by means of a process in which a sintering step is followed by a solution treatment step, with the alloy being cooled from a sintering temperature to a solid solution treatment temperature in a controlled manner such that all the alloying elements are put into uniform solid solution.

It has been found that such controlled cooling from the sintering temperature to the solid solution treatment temperature enables all the constituents to be dissolved into a homogeneous solid solution and enables improved magnetic properties to be obtained in an $\text{Sm}_2\text{CO}_{17}$ alloy. For example, it is possible for the alloy to have a relatively high iron content (to provide high remanent induction) without the 2-17 Sm-Co phase being rendered unstable, and to have a relatively high samarium content to provide good second quadrant loop squareness. With prior art processes, it was found that the presence of a high iron content causes the required 2-17 Sm-Co rhombohedral phase to become unstable, with resultant transformation to iron-rich phases and consequent deterioration of magnetic properties, especially remanent induction.

By using such a process it is possible to produce a permanent magnet which attains its specified properties in a magnetizing field of about 25 kOe, has an energy product $(BH)_{\text{max}}$ of at least 30 MGOe and has a satisfactory intrinsic coercivity iH_c of 14-16 kOe. A magnet in accordance with the present invention can also have a satisfactory remanent induction B_r of at least about 11.5 kG and a better loop squareness in the second quadrant, i.e. H_K of approximately 9.0 kOe.

It has been found that the initial alloy body should be sintered at the highest possible temperature in the liquid + solid region to achieve full density and high remanent induction. The sintering temperature may be at least about 1200°C at at least the end of the



sintering step. The sintering temperature should be such that the alloy consists at that temperature of a mixture of liquid and solid phases to promote rapid sintering. The predominant solid phase consists of 2-17 Sm-Co
5 grains, with these being surrounded by a liquid phase comprising a CuSm phase which also contains a small amount of a Zr-rich phase.

The sintering process may be carried out in an inert atmosphere such as argon, or in hydrogen or in a
10 vacuum, or in a combination of these. In the case of sintering solely in an atmosphere of argon the possibility exists that some argon may be trapped in pores within the sintered alloy. This undesirable occurrence can be minimized by sintering initially at a somewhat
15 lower temperature in a vacuum so as to decrease the porosity and then increasing the temperature in an argon atmosphere to achieve full density. Similarly it is not practical to sinter entirely in a vacuum as excessive loss of samarium would result and the preferred procedure
20 would be to sinter initially at a lower temperature in a vacuum and then change to an argon atmosphere before raising the temperature to the desired higher level. Alternatively the alloy may be sintered initially in an atmosphere of hydrogen at a somewhat lower temperature,
25 for example 1150°C for 30 min, to close the internal porosity, followed by heating to the range of 1200-1215°C in an atmosphere of argon and holding at that temperature for 10 min.

In accordance with the invention, the sintered
30 alloy body is cooled in a controlled manner from the sintering temperature to a solid solution treatment temperature to ensure homogeneous equilibrium dissolution of the CuSm and Zr-rich phases into solid solution in the stable 2-17 Sm-Co phase. A relatively high iron content
35 renders such dissolution more difficult to achieve since

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the high iron content reduces the temperature range within which the stable 2-17 Sm-Co solid phase exists as a single phase. However, the controlled cooling from the sintering temperature to the solution treatment temperature in accordance with the invention enables this problem to be overcome.

If a sintered alloy body with relatively higher iron content is cooled too rapidly from the sintering temperature to the solid solution treatment temperature, the CuSm and Zr-rich phases remain concentrated at the grain boundaries. The localized high concentration of samarium results in transformation of the 2-17 Sm-Co phase to an Fe-rich phase with lower remanent induction. Also, in the same grain boundary region, zirconium may be rejected from solid solution, with a resultant adverse effect on loop squareness. The possibility of occurrence of such undesired effects is significantly reduced by slow cooling from 1170°C to the solid solution treatment temperature in accordance with the present invention.

After slow cooling to the solid solution treatment temperature, which is marginally below the solid+liquid/solid phase transformation temperature for the alloy composition and which may for example be from about 1140 to about 1150°C, the alloy body is maintained at this temperature for a period of time (for example about 2 hours) to improve the dissolution of the alloying elements and to remove any structural faults by annealing. The alloy body is then quenched from the solid solution treatment temperature to a temperature below 800°C at a rate of about 10°C/s, and thereafter to room temperature. In our co-pending application it is disclosed that optionally part of the samarium may be replaced by praseodymium. In this case the solid+liquid/solid phase transformation temperature will be lower and the solid solution treatment temperature must be lower,

in the range 1120-1145°C.

The alloy body is then aged to develop the 1-5 Sm-Co phase network. The aging temperature will be generally in the range of 800-860°C but must be precisely
5 chosen depending on the composition, in particular on the zirconium content. A preferred aging temperature in the present invention is 845±5°C for 20 hours.

After the aging step, it is necessary to cool the alloy body in a controlled manner to effect the
10 required magnetic hardening, that is to say achieve the required intrinsic coercivity and good loop squareness. Such controlled cooling may be from the aging temperature to about 600°C at a rate preferably about 2°C/min and from about 600°C to the secondary aging temperature in
15 the region of 400°C at about 1°C/min. A preferred secondary aging treatment in the present invention is 410°C for 10 hours. The alloy body is then cooled to room temperature.

It is postulated that during cooling from the
20 first aging temperature and during holding at the second aging temperature regions of 2-17 Sm-Co phase nucleate coherently within the 1-5 Sm-Co phase network thereby creating lattice strain and magnetic hardening⁽¹⁶⁾. When magnetically hardened, the 1-5 Sm-Co phase network
25 serves as a barrier to magnetic domain wall motion and creates the required intrinsic coercivity and good second quadrant loop squareness.

An alloy body in accordance with one embodiment of the invention was produced in preliminary form with
30 the following composition by weight: 22.7% effective Sm, 22.0% Fe, 4.6% Cu, 1.5% effective Zr, and balance cobalt. The alloy body was sintered for 30 min in hydrogen at 1150°C, and for 10 min in argon at 1205°C. The sintered alloy body was then cooled to 1150°C at a
35 rate of 2°C/min.

The alloy body was then subjected to solid solution treatment at a temperature of 1140 to 1150°C for 2 hours. After the solid solution treatment, the alloy body was quenched to room temperature. A micrograph showed that a uniform single phase solid solution structure was achieved.

The alloy body was then aged by reheating to 815°C and maintained at that temperature for 20 hours, then the alloy body was cooled to 600°C at a rate of 2°C/min and from 600° to 410°C at a rate of 1°C/min, held at 410°C for 10 hours and then cooled to room temperature. A micrograph was taken and showed a uniform structure of 2-17 Sm-Co grains.

Another alloy body having the same composition as the previous alloy body was prepared and subjected to the same treatment as the previous alloy body, except that cooling from the sintering temperature to the solid solution treatment temperature was effected at a rapid rate of 10°C/s. The alloy was then reheated to 815°C and aged as described above. A micrograph was taken and showed large grains constituting the 2-17 Sm-Co phase, with a CuSm black phase and a Zr-rich white phase being seen in the grain boundary area.

The alloy bodies were then magnetized in a magnetizing field of 25 kOe and the resulting magnetic properties were measured, as shown in the following Table.

	B_r (kG)	iH_c (kOe)	H_K (kOe)	$(BH)_{max}$ (MGoe)
Slow cooling	11.7	15.8	9.0	30.8
Rapid cooling	11.7	14.9	6.0	28.0

The superior magnetic properties of the alloy body which was subjected to slow cooling from the sintering temperature to the solid solution treatment temperature in accordance with the invention are readily apparent.

It was found that in the sintering process it is advantageous to sinter first in an atmosphere of hydrogen followed by a further period in an atmosphere of argon. For example, a preferred sintering process is to
5 sinter for 30 min in hydrogen at 1150°C, change the furnace atmosphere to argon, increase the temperature at 4-5°C/min to 1205°C and maintain this temperature for 10 min. It was observed that during the first sintering treatment the density of the product increases by pore
10 closure with entrapment of some hydrogen. In the second sintering treatment in argon the internal hydrogen is removed by diffusion and the remaining pores are closed to full density. No argon entrapment occurs during the second sintering treatment as the external porosity has
15 been sufficiently closed by the initial sintering treatment, and no hydrogen remains in the alloy as the final sintering treatment is carried out in argon. If the entire sintering treatment is carried out in argon, some argon is trapped within the internal porosity and
20 results in residual porosity, lower density and lower remanence (B_r) in the finished magnet.

To achieve improved magnetic properties, e.g. higher energy product, systematic increases were made in the Fe content and it was found that it was necessary to
25 adjust the other elements accordingly and to adjust the temperature and time of the solution heat treatment to achieve the basic requirement of putting all the alloying elements into uniform solid solution. For example, to increase the Fe content from 15% to 22% it was also
30 necessary to reduce the Cu content from 6.0% to 4.6% and the effective Zr content from 2.5% to 1.5% and to modify the solution heat treatment from one hour at 1180°C to a controlled cooling procedure from the sintering temperature of 1205°C to the solution heat treatment temperature
35 which is marginally below the solid+liquid/solid phase

transformation temperature. This temperature is dependent upon the precise composition and may be determined metallographically. The major influence on this transformation temperature is that observed for iron, for example, for alloys containing 15% Fe the transformation temperature was determined to be 1180°C, for 17% Fe, 1170°C and for 22% Fe, 1150°C, i.e. there is approximately 4°C decrease in transformation temperature for 1% Fe increase in the range studied to date.

Following solution treatment, the alloy is quenched to room temperature and reheated to the aging temperature in the range of 800-860°C for up to 20 hours. In this aging treatment the 2-17 Sm-Co solid solution transforms into a duplex structure consisting of a continuous network of 1-5 Sm-Co phase within the 2-17 Sm-Co matrix. We have found that this broad range of 800-860°C for the aging temperature is not acceptable and that the aging temperature must be precisely determined with respect to the zirconium content. For example, the optimum aging temperature was found to be $815 \pm 5^\circ\text{C}$ for an effective zirconium content of 2.0-2.5%. For lower zirconium contents the aging temperature must be raised. For example, the optimum aging temperature was found to be $845 \pm 5^\circ\text{C}$ for an effective zirconium content of 1.4-2.0%. It was found that a minimum time of about 20 hours is required at the aging temperature to form the required 1-5 Sm-Co phase network to develop the desired coercivity. Shorter times, i.e. 10 and 15 hours, result in lower coercivities and longer times, i.e. 30 hours, do not produce any further improvements. To develop the required coercivity and loop squareness (H_K) it is necessary to have a continuous network of the 1-5 Sm-Co phase. This requires sufficient samarium to be present and we have found 22.5-23.5% effective samarium to be a preferred amount.

In this aging treatment, it has been observed that the nature of the structural change taking place is critically dependent upon the temperature at which the aging process is started, that is to say the same result cannot be obtained by using a higher temperature for a shorter time or vice versa. This behaviour is typical of a spinoidal decomposition as distinct from a nucleation and growth reaction.

Following this primary aging treatment at 800-860°C the specimen must be cooled to the secondary aging temperature in the range 400-425°C at a critical rate. The preferred cooling rate is about 2°C/min from the aging temperature to about 600°C and about 1°C/min from about 600°C to the secondary aging temperature. Small variations to the above do not appear to have a deleterious effect, however cooling rapidly such as >2°C/min or very slowly such as <0.5°C/min resulted in inferior magnetic properties. It is postulated that during this critical cooling step regions of 2-17 Sm-Co phase nucleate coherently within the 1-5 Sm-Co phase network, thereby causing lattice strain and creating the coercivity(16). This transformation is enhanced by the presence of copper in the 1-5 Sm-Co phase. From this model it is understood that faster cooling rates do not permit regions of the 1-5 Sm-Co phase to transform to the 2-17 Sm-Co phase, and slower cooling rates allow incoherent nucleation to take place without lattice strain.

In the 1-5 Sm-Co system containing copper, the aging process to develop coercivity shows an optimum temperature in the range of 400-450°C(16). It was found that in 2-17 Sm-Co magnets in accordance with the mechanism in which coercivity and loop squareness (H_K) are being developed by aging the 1-5 Sm-Co phase network containing copper, the same effect applies. The optimum aging

temperature was found to be 410-415°C. With an aging temperature of 400°C for 10 hours a lower loop squareness (H_K) was obtained as was also the case at 422°C, as shown below.

5	Aging	Composition			
	Temperature	Sm	Cu	Fe	Zr
	°C	23.0	4.6	22	1.9
		H_K (kOe)			
	400		7.6		
10	410		8.7		
	422		7.8		

It has been found that an aging treatment of 10 hours at 410-415°C is effective. It is also believed that the optimum secondary aging temperature is dependent upon the copper content.

It was found that the final cooling step to room temperature after aging at 400-425°C is not critical.

The present invention also provides a process for producing an $\text{Sm}_2\text{Co}_{17}$ alloy permanent magnet, containing also iron, copper and zirconium or a similar group IVB or VB transition metal, the process comprising: providing said alloy in a preliminary form, sintering said alloy at an elevated temperature to achieve a high density which results in a high remanence, selecting a solution treatment temperature which is marginally below the liquid+solid/solid phase transformation temperature for the preferred composition of said alloy, cooling the alloy from the elevated sintering temperature to the solution treatment temperature in a controlled manner such that all the alloy constituents are put into a uniform solid solution, holding at the solid solution treatment temperature, quenching the alloy to room temperature, reheating the alloy to the aging temperature, which is critically dependent on the composition of

said alloy, particularly the zirconium content, and holding for sufficient time for the 2-17 Sm-Co solid solution to transform into a structure consisting of a continuous network of the 1-5 Sm-Co phase within the 2-17 Sm-Co matrix, cooling said alloy to the secondary aging temperature at a critical rate and holding at that temperature for a specified time such that regions of 2-17 Sm-Co phase nucleate coherently within the 1-5 Sm-Co phase network thereby creating lattice strain which results in high coercivity and good loop squareness, and cooling said alloy from the secondary aging temperature to room temperature.

The following comments in connection with the invention are also appropriate:

1. A high sintering temperature develops a high density and this results in ultimately a high remanence. To minimize distortion a two stage process is preferred; 30 min in hydrogen at 1150°C followed by heating in argon at 4-5°C/min to 1205°C and holding at this temperature for 10 min.
2. A high iron content is desirable to increase the remanence and energy product but the copper and zirconium contents must be reduced as the iron is increased to maintain the uniform 2-17 Sm-Co solid solution. Iron has the most marked effect on the solution treatment temperature. A preferred amount is 22% Fe and a preferred solution treatment temperature is 1140-1170°C.
3. Samarium and zirconium must be regarded as "effective" amounts to allow for the presence of oxygen and carbon respectively, as taught in our co-pending application.
4. Sufficient samarium must be present to ensure that when the 1-5 Sm-Co phase network is formed within the 2-17 Sm-Co matrix in the aging process, the 1-5 Sm-Co

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phase network is continuous. This is necessary for good coercivity and loop squareness (H_K). A preferred amount of effective samarium is 23.0%.

5. The effective zirconium present has a critical effect on the precise temperature at which the above aging transformation takes place. A preferred amount of effective zirconium is 1.4 to 2.0% with aging treatments of $845 \pm 5^\circ\text{C}$ - $815 \pm 5^\circ\text{C}$ respectively for 20 hours.

6. The copper present influences beneficially the final transformation of regions of the 1-5 Sm-Co phase network into coherent regions of 2-17 Sm-Co phase during the controlled cooling from the primary aging temperature in the range of 800 - 860°C to the secondary aging temperature and the holding at that temperature. The coherent regions of 2-17 Sm-Co phase distort or strain the 1-5 Sm-Co phase network which results in high coercivity. A preferred amount of copper is 4.6%. A preferred cooling rate is $2^\circ\text{C}/\text{min}$ from 860°C to 600°C and $1^\circ\text{C}/\text{min}$ from 600°C to 410°C . A preferred secondary aging temperature is 410°C . A preferred holding time at 410°C is 10 hours.

7. As stated earlier, both zirconium and copper levels must be controlled to permit the iron level to be optimized whilst still permitting all the alloying elements to go into uniform solid solution in the solution treatment step.

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CLAIMS

1. An $\text{Sm}_2\text{CO}_{17}$ alloy characterised in that it contains a first or effective amount of Sm in the range 22.5 to 23.5%, from 20.0 to 25.0% Fe, from 3.0 to 5.0% Cu, a first or effective amount of Zr in the range 1.4 to 2.0%, a minor amount of oxygen and a minor amount of carbon, a second or additional amount of Sm in the range of from 4 to 9 times the oxygen content of the alloy, a second or additional amount of Zr in the range of from 5 to 10 times the carbon content of the alloy, said percentages being on a weight basis and the balance being cobalt, the said alloy having a crystallographic structure comprising cells of 2-17 Sm-Co rhombohedral phase surrounded by a continuous network of the 1-5 Sm-Co hexagonal phase.
2. An alloy according to claim 1, containing 23.0% Sm as said effective amount of Sm, 22.0% Fe, 4.6% Cu, and 1.5% Zr as said effective amount of Zr.
3. An alloy according to claim 1 or 2, wherein the additional amount of Sm is 6.265 times the oxygen content of the alloy.
4. An alloy according to claim 1, 2 or 3, wherein the additional amount of Zr is 7.595 times the carbon content of the alloy.
5. An alloy according to claim 1 or 2, wherein some of the samarium is replaced by praseodymium.
6. An alloy according to claim 5 as dependent on claim 2 wherein said 23% Sm is replaced by 20% Sm and 2.5% Pr.
7. An alloy according to claim 5 or 6, wherein the additional amount of Sm is 5.871 times the oxygen content.
8. An alloy according to claim 1 or 2 wherein at least some of the zirconium is replaced by another group IVB or VB transition element.
9. An alloy according to claim 8, wherein the said effective amount of

Zr is completely replaced by 2.7-4.0% Hf and the additional amount of zirconium is completely replaced by an additional amount of hafnium in the range of from 10 to 20 times the carbon content of the alloy.

10. An alloy according to Claim 9, wherein the additional amount of Hf is 14.862 times the carbon content of the alloy.

11. An alloy according to any one of claims 1-10, wherein the oxygen content of the alloy is not greater than 0.6% by weight.

12. An alloy according to any one of claims 1-11, wherein the carbon content of the alloy is not greater than 0.1% by weight.

13. A permanent magnet comprising an alloy as claimed in any one of the preceding claims.

14. A process for producing an $\text{Sm}_2\text{CO}_{17}$ alloy as claimed in any one of claims 1-12, characterised in that the process comprises:-

providing the alloy in a preliminary form,

sintering the preliminary alloy at an elevated temperature to achieve a high density and high remanence,

cooling the sintered alloy body from the sintering temperature to the solution treatment temperature in a controlled manner to put the alloy constituents into a substantially uniform 2-17 Sm-Co solid solution, said solution treatment temperature being marginally below the solid + liquid/solid phase transformation temperature of said alloy,

holding the alloy at the solid solution treatment temperature,

quenching the alloy to room temperature,

reheating the alloy to a first aging temperature to transform the 2-17 Sm-Co solid solution into a structure comprising a network of the 1-5 Sm-Co phase within a 2-17 Sm-Co matrix,

cooling the alloy to a second aging temperature in a controlled manner to cause regions of 2-17 Sm-Co phase to nucleate coherently within the 1-5 Sm-Co phase network and create lattice strain which results in high coercivity and good loop squareness, and

recooling the alloy to room temperature.



European Patent
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EUROPEAN SEARCH REPORT

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Application number

EP 85 30 0957

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	GB-A-2 089 371 (K.K. SUWA SEIKOSHA) * Claims 1,2,7; examples 1,7,8 *	1,2,8	C 22 C 19/07 H 01 F 1/04
A	--- GB-A-2 021 147 (K.K. SUWA SEIKOSHA) * Claims 1,2 *	1,8	
A	--- DE-A-2 944 031 (K.K. SUWA SEIKOSHA) * Claims 1,2,5 *	1,5,8	
A	--- DE-A-2 727 243 (HITACHI METALS) * Claims 1,5,6 *	1,8	
A,D	--- US-A-4 221 613 (IMAIZUMI et al.) * Claim 1 * & US - E - 31 317	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A,D	--- US-A-4 172 717 (TOKUNAGA et al.) * Claims 1,2 *	1	C 22 C 19/07 H 01 F

The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 13-06-1985	Examiner LIPPENS M.H.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			