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## Modern magnetic materials - the review

**Streszczenie.** W artykule przedstawiono współczesne materiały magnetyczne. Opisano materiały magnetycznie miękkie - żelazo, stopy żelaza, blachy elektrotechniczne, stopy NiFe, ferryty, materiały amorficzne i na nanokrystaliczne. Opisano też materiały magnetycznie twarde - Alnico, ferryty, materiały na bazie ziem rzadkich. (**Współczesne materiały magnetyczne - przegląd**).

**Abstract.** The paper reviews modern magnetic materials. As soft magnetic materials it has been described - iron, iron cobalt alloys, iron aluminum alloys, SiFe electrical steels, NiFe alloys, soft ferrites, amorphous and nanocrystalline alloys. As hard magnetic materials there are described - Alnico alloys, hard ferrites and rare-earth metals based alloys.

**Słowa kluczowe:** materiały magnetyczne miękkie, blachy elektrotechniczne, materiały magnetyczne twarde.

**Keywords:** soft magnetic materials, hard magnetic materials, electrical steel, amorphous and nanocrystalline alloys.

### Introduction

Commonly as *magnetic materials* we consider the ferromagnetic or ferrimagnetic materials although also other materials (diamagnetic and paramagnetic) exhibit magnetic properties. This magnetic materials are divided into two clearly separated class of materials - *soft magnetic materials* and *hard magnetic materials*. As a criterion it is assumed the coercivity - IEC Standard 404-1 proposed the coercivity 1 kA/m as a value to distinguish both groups of products. This border is rather symbolic because both classes are completely other - from soft magnetic materials we require as small as possible coercivity (even part of A/m - not larger than 100 A/m) while hard magnetic materials should have coercivity as large as possible (larger than 100 kA/m). Recently on the market appear intermediate class of hard magnetic materials called *semi-hard magnetic materials* (with coercivity between 1000 and 100 000 A/m). Fig. 1 presents the range of magnetic materials taking into account coercivity.

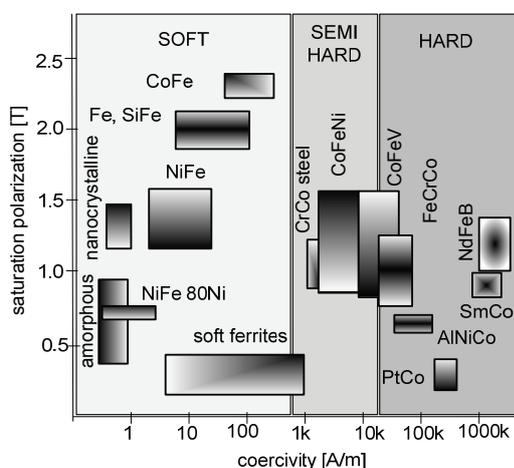


Fig. 1. The range of market available magnetic materials (as an example products offered by Vacuumschmelze)

*Soft magnetic materials* cover huge market of various products - about  $7 \times 10^6$  tons annually and about  $10^{10}$  Euro [1]. We can divide these products taking onto account magnetic performances, application, cost and other properties. Even in the case of SiFe electrical steel the best grade can be more than ten times expensive than ordinary grades. And between cheap ferrites and high quality soft magnetic materials these differences in cost are much larger.

Taking into account importance of various groups of soft magnetic materials it should be noted that almost 80% of the market occupies SiFe electrical steel (Fig. 2). With ferrites and permalloys (NiFe) it is more than 95% and we see that other materials, including amorphous and nanocrystalline are marginal in value.

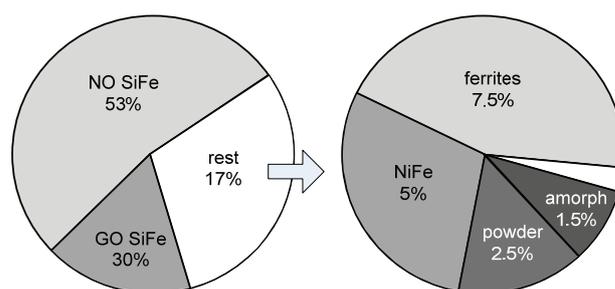


Fig. 2. Annual value of world production of soft magnetic materials (after [2])

After introduction of *rare-earth metals* as neodymium and samarium to production of permanent magnets (and after more wide exploitation of deposits of the main minerals containing these elements - monazite, bastnázite in China and Brasil) it is observed significant progress in quality of permanent magnets.

Historically first as hard magnetic materials were used different kinds of steel. In 1917 in Japan was developed cobalt steel ( $Fe_{55}Co_{35}W_7Cr_2C_{0.6}$ ) known as Honda alloy. In 1931 was developed in Japan by Mishima Alnico alloy

( $\text{Fe}_{58}\text{Ni}_{30}\text{Al}_{12}$ ) of much better performances in comparison with steel. Recently cobalt steel practically is vanished from the market as material for permanent magnets. Fig. 3 presents the market of permanent magnet materials

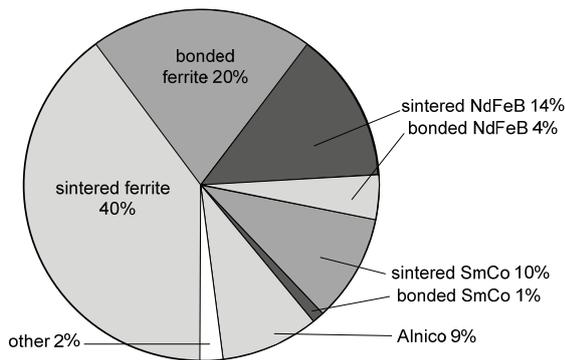


Fig. 3. Permanent magnet market (1995) - after [3]

### Soft magnetic materials

Depending on application various performances of soft magnetic materials are required. In the case of electric power devices: power and distribution transformers, electric machines the most important factors are: small power loss and large saturation polarization. If we would like to choose between silicon steel and amorphous materials (neglecting other factors) we meet contradiction - amorphous materials exhibit smaller power loss but also significantly smaller saturation polarization. Table 1 presents the competition of parameters of the representative of the main soft magnetic materials.

Table 1. Competition of parameters of the representative of the main soft magnetic materials

Parameter	3% SiFe GO	FeSiB Metglas	Ni80Fe20 Permalloy	Co50Fe 50 Permen dur	MnZn Ferrite
$B_s$ [T]	2.03	1.56	0.82	2.46	0.2 - 0.5
$H_c$ [A/m]	4 - 15	0.5 - 2	0.4 - 2	160	20 - 80
P1.5T/50Hz [W/kg]	0.83	0.27		1	
P 1T/1kHz [W/kg]	20	5	10	20	
$\mu_{max} \times 1000$	20 - 80	100 - 500	100 - 1000	2 - 6	3 - 6
Frequency range [kHz]	3	250	20		2000 NiZn - 100 000

If magnetic material is used for shielding losses are not as important as permeability and amorphous materials or permalloy are advisable. In the case of high frequency applications beside losses important is deterioration of magnetic properties (for example permeability) with frequency - we see that in this case the materials are ordered as follows: SiFe - NiFe - amorphous/nanocrystalline - MnZn ferrite - NiZn ferrite (in microwave range - garnets).

The specially important are CoFe alloys - the material of the largest saturation polarization available - 2.46 T. Fig. 4 presents the diversity of market available soft magnetic materials.

### Iron and iron alloys

Pure iron has excellent magnetic performances: large saturation polarization  $J_s = 2.15$  T, small coercivity  $H_c = 3 - 12$  A/m and large permeability  $\mu_{max} = 280\ 000$  (single crystal magnetically annealed even 1 400 000). But main problem is that such performance has extremely pure iron - even small presence of impurities causes significant deterioration of magnetic properties (Fig. 5). Therefore such extremely pure material is rather expensive and possible to use only in laboratory.

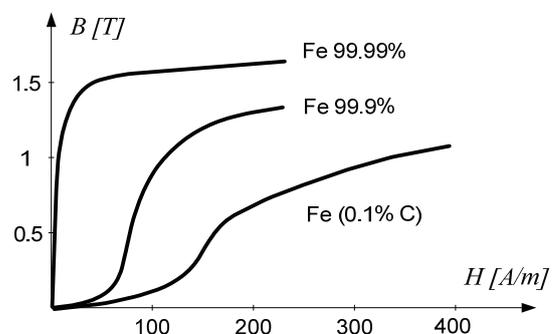


Fig. 5. Magnetization curves of iron (after [39])

Commercially available pure iron has much smaller permeability  $\mu_{max} = 10\ 000 - 20\ 000$  and larger coercivity  $H_c = 20 - 100$  A/m because impurities as C, Mn, P, S, N, O are pinning the domain wall motion. By annealing such material in hydrogen at 1200 - 1500 °C it is possible to remove these impurities but also such process is expensive.

Pure iron has small resistivity  $\rho = 10 \mu\Omega\text{cm}$  (in comparison with 45  $\mu\Omega\text{cm}$  of GO SiFe and 140  $\mu\Omega\text{cm}$  of amorphous material). Such good conductivity causes large eddy current loss and practically preclude pure iron for AC application.

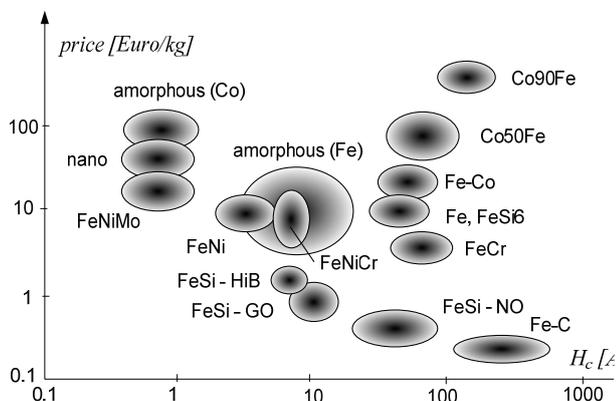


Fig. 4. Diversity of soft magnetic materials (after [4])

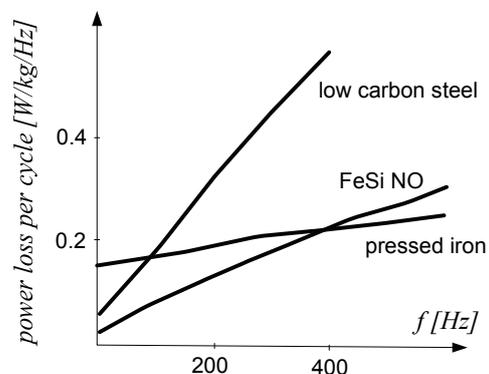


Fig. 6. Power loss of various iron based materials (after [5])

Both problems - expensive manufacturing and limited frequency application can be solved if we use the same material in form of a *powder iron*. This material is manufactured by grinding iron (or iron alloys<sup>1</sup>) into powder with dimension of particles 5 - 200  $\mu\text{m}$  and next by pressing this powder with insulating material. Resistivity of such material is of the order of  $\rho = 10^4 \mu\Omega\text{cm}$  and therefore it can be used in high frequency range to 100 kHz (specially prepared NiFe powder to 100 MHz) [6].

Instead of cheap pressing technology most often is used sintering technology resulting in better magnetic performances of the powder materials. As a material for powder iron cores most commonly is used *carbonyl iron*. Technology of obtaining extra pure iron powder from iron pentacarbonyl  $\text{Fe}(\text{CO})_5$  was developed in 1925 by BASF Company. By thermal decomposition of iron pentacarbonyl it is possible to produce 99.8% pure iron powder with spherical particles ranging from 1 to 8 microns.

Although presence of carbon significantly deteriorate magnetic properties of iron (Fig. 6) *low carbon steel* is widely used as magnetic material mainly due to low price and good mechanical properties. As low carbon steel it is assumed the electrical steel with acceptable impurities: C - 0.04 - 0.06%, P - 0.05 - 0.15%, Mn - 0.35 - 0.8%, S - 0.006 - 0.025%, Si - 0.05 - 0.25%. Although the magnetic properties of low carbon electrical steel are rather poor they are acceptable for many cheap device, as: small motors, relays or electromechanical mechanisms.

Especially important are alloys Fe-Co because alloys Fe50Co50 (known as *Permendur*) exhibits the largest possible saturation polarization  $J_s = 2.46 \text{ T}$  and very large Curie temperature  $T_c = 930 \text{ }^\circ\text{C}$ . To improve mechanical properties of FeCo alloy (and enlarge of the resistivity  $\rho = 40 \mu\Omega\text{cm}$ ) a small part of vanadium is added: Fe49Co49V2. The alloy Fe6Co94 has very large Curie temperature  $T_c = 950 \text{ }^\circ\text{C}$  (pure cobalt has  $T_c = 1130 \text{ }^\circ\text{C}$ ). Table 2 collects performances of iron and its alloys.

Table 2. Performances of iron and iron-alloy materials

	$H_c$ [A/m]	$\mu_{\text{max}} \times 1000$	$J_s$ [T]
99.95 Iron	4	230	2.15
Iron (commercially)	20 - 100	4 - 20	2.15
Carbonyl (powder)	6	20	2.15
CoFe2%V (Permendur)	200	3	2.4
Low carbon steel C - 0.04 - 0.06%	Power loss 5.5 - 10 W/kg at 1.5 T 50 Hz		

### Silicon steel

#### The conventional grain oriented (CGO) SiFe steel

The two invention were a turning points in history of improvement of soft magnetic materials: addition of Si and Goss texture. The first invention was proposed by Robert Hadfield in 1902 [7] and patented in 1903 [8]. The second invention was patented by Norman Goss in 1934 [9] and described in 1935 [10].

The most important drawback of pure iron is relatively low resistivity and the same large eddy current loss. Commonly to decrease the resistivity the small part of Si is added. Addition of silicon influences saturation polarization and Curie temperature (Fig. 7).

From Fig. 7 is clear that the best would be 6.5% content of Si because resistivity increases almost sevenfold and the material on non-magnetostrictive. Unfortunately such material is very brittle what is disadvantageous in rolling process as well in punching ready to use steel. The

punching capability is the best for 3 - 4% silicon content. Large content of Si causes also decrease of saturation polarization and the same permeability. Therefore recently GO silicon steel is manufactured most often with 3 - 3.3 % of silicon although also 6.5% SiFe is offered on the market (in small volume and for higher price).

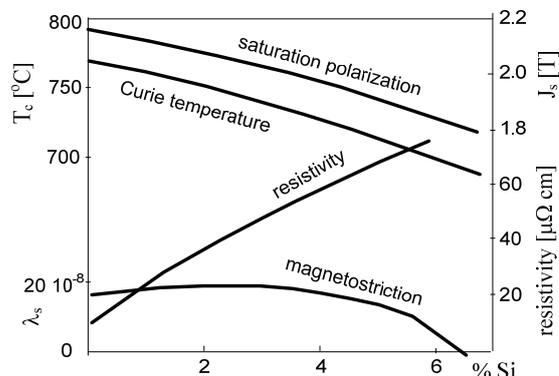


Fig. 7. Magnetic and electrical parameters as a function of silicon content

In a grain oriented steel we profit the anisotropic properties of the iron crystal and the fact that this crystal have the best magnetic properties in "easy" [100] direction. Therefore the main effort are taken to obtain the best Goss texture with relative large grains ordered in one direction. Fig. 9 presents dependence of loss on the tilt angle. Surprisingly to obtain minimum of the loss the best is not the perfect grain orientation. The best results is for the grain orientation of about 2°.



Fig. 8. The example of typical grain structure of GO steel - in the left part visible non completely recrystallised line

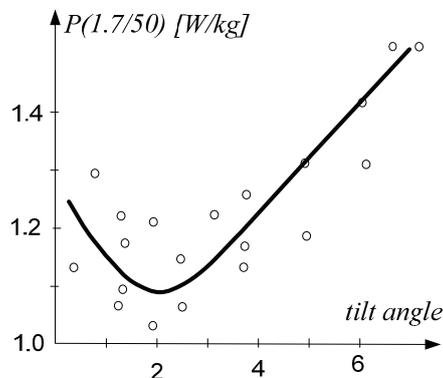


Fig. 9. Core loss versus the tilt angle [11]

<sup>1</sup> In powder materials also other substances, as NiFe or Sendust are used.

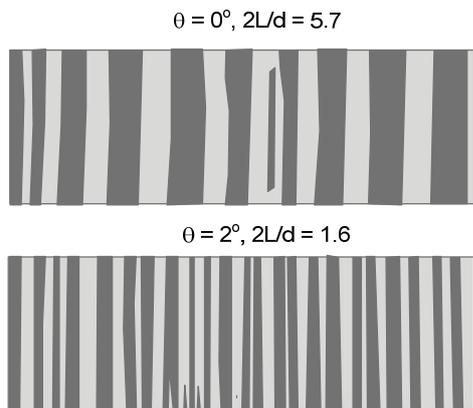


Fig. 10. Domain structure of 3% Si-Fe crystals ( $\theta$  - tilt angle,  $2L$  - domain wall spacing,  $d$  - thickness) (after [12])

Partially results presented in Fig. 9 explain results of domain investigations presented in Fig. 10. Perfectly oriented grain have more wider  $180^\circ$  domain wall spacing than the same for tilt angle  $2^\circ$ . This domain width strongly influences excess loss.

After first annealing in production process the grains dimensions are only around 0.02 mm. After second annealing (secondary recrystallization) the Goss-oriented grains grow through the thickness of the sheet to diameter 3 - 7 mm with average misorientation about  $6^\circ$ .

Theoretically as larger grains as better. But measurements of loss versus grain dimensions did not confirm such simple relation. Indeed domain observation confirm that large grains have a wide domain spacing [13]. That is why usually grain diameter in conventional GO steel rather not exceeds about 8 mm.

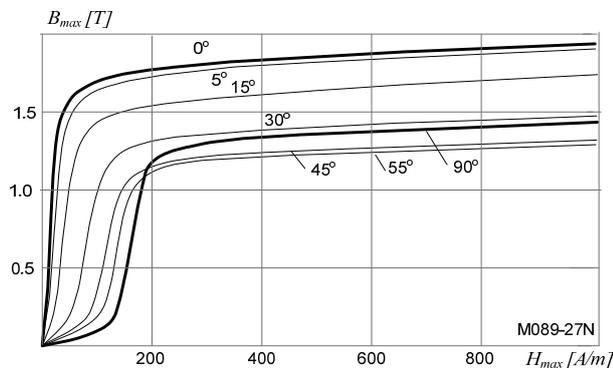


Fig.11. Magnetization curves of the GO SiFe steel in different directions of magnetization (with respect to rolling direction)

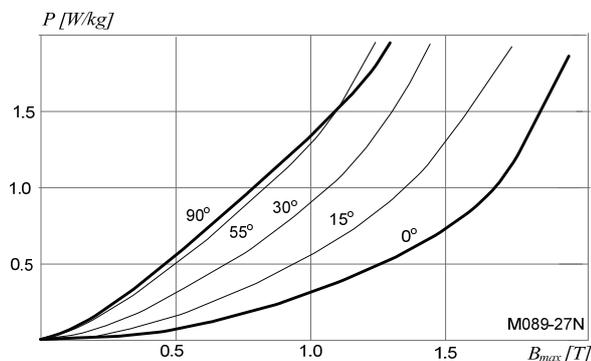


Fig.12. Power loss of the GO SiFe steel in different directions of magnetization (with respect to rolling direction)

Excellent properties along rolling direction are advantageous when we can guarantee that magnetization is only in this direction. But this advantage can be a problem when exist part magnetized not exactly in the rolling direction (for example corners of the yoke). In such case we have to expect significant deterioration of the material performances. Figs. 11,12 present the magnetization curve and losses determined for other than the rolling direction.

Electrical GO steel is classified according to international standards basing on the power loss. European standard EN 10107 uses [following names to order the steel grades: 1) first letter M for electrical steel; 2) last letter : N - normal, S - reduced loss, P - high permeability; 3) after first letter: value of specific power loss for 1.5 T (material N) or for 1.7 (material S or P), 4) before last letter: thickness. For example M097-30N means normal material of the thickness 0.3 mm and 1.5 T/50 Hz and power loss not exceeding 0.97 W/kg. Fig. 13 presents parameters of the typical GO SiFe steel - grade: M089-27N

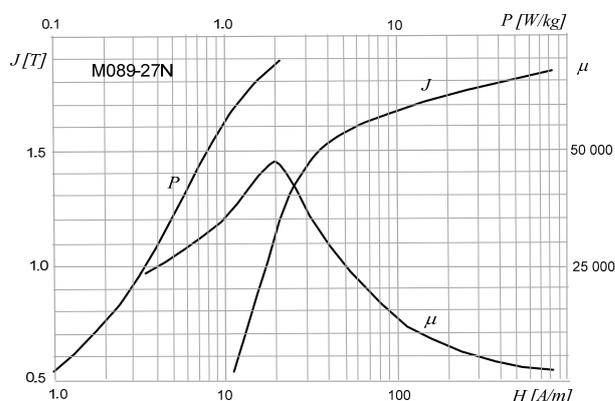


Fig. 13. Parameters of the typical GO SiFe steel - grade: M089-27N

### HiB grain oriented electrical steel

The conventional GO SiFe steel has Goss texture [001] (110) with grain orientation dispersion (tilt angle) of about  $6^\circ$ . In 1965 Nippon Steel Corporation developed new technology of producing of GO SiFe steel [14,15,16]. After addition of around 0.025% aluminum to the starting melt the recrystallization process was enhanced due to aluminum nitride AlN acting as inhibitor. The production route was simplified - hot rolled material was initially annealed at  $1100^\circ\text{C}$  in  $\text{N}_2$  and in one cycle cold rolled to final thickness. Next conventional procedure is performed - decarburization, batch annealing for recrystallization at  $1200^\circ\text{C}$  and final  $800^\circ\text{C}$  annealing.

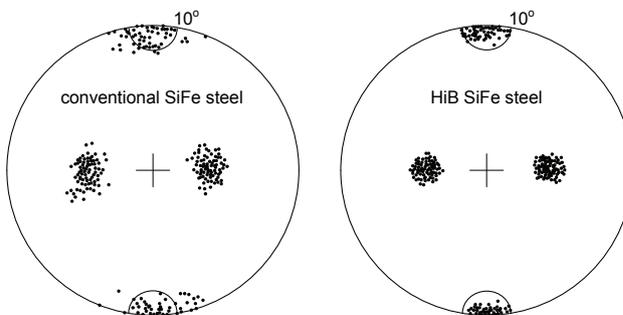


Fig. 14. (100) pole figures [15]

As result was obtain new class of material with more perfect texture - tilt angle  $2-3^\circ$  and grain dimensions exceeding 10 mm. This material exhibits significantly smaller losses for large polarization (above 1.7 T) and this flux density was for significantly smaller magnetic field strength. Therefore it is known as HiB or high permeability material. Fig. 14 presents the comparison of pole figures determined for HiB and conventional steel.

Similar new technology introduced in 1973 Kawasaki Steel using as inhibitor MnSe + Sb and in 1975 Allogheny Ludlum Steel Corporation using as inhibitor addition of boron. These Kawasaki technology has two cycles of cold rolling [17,18,19].

It should be noted that better performances of HiB steel are especially revealed for high polarization (according to the name). For small polarization advantages of HiB steel are not so evident - sometimes this material can be comparable or even worse than conventional steel. Fig. 15 presents the typical parameters of HiB steel.

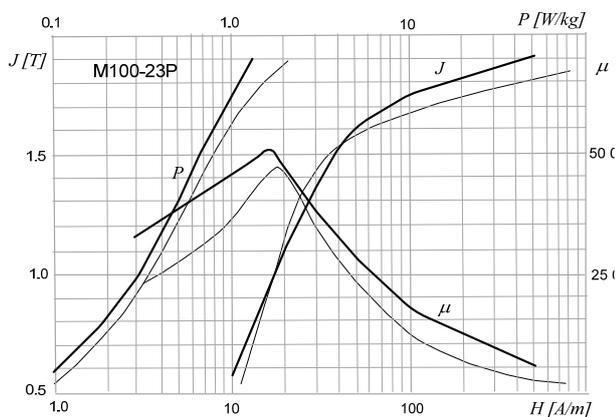


Fig. 15. Parameters of the HiB GO SiFe steel - grade: M100-23P (thin line - the same parameters of conventional steel for comparison)

The effect of perfect grain orientation can be weakened by wide domain wall spacing. Therefore HiB steel is often supports by domain refinement tools - laser scribing, plasma jet irradiation, spark ablation, groove making, chemical treatment or coating stress. Recently most commonly used technique is laser scratching (sometimes supported by stress coating or chemical etching).

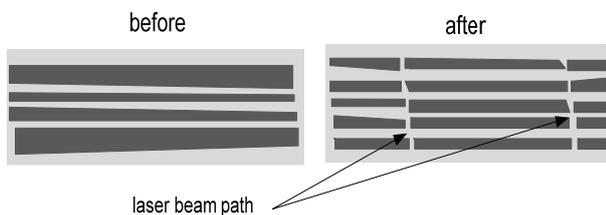


Fig. 16. Domain structure after laser scribing

Usually the high power laser beam focused onto a 150  $\mu\text{m}$  makes scribed line transversely to the rolling direction with scratch distance of about 5 mm. Fig. 17 presents the example of result of laser scratching technique. After application of domain refinement it is possible to obtain the core loss 5 - 10% lower than the untreated high permeability steel.

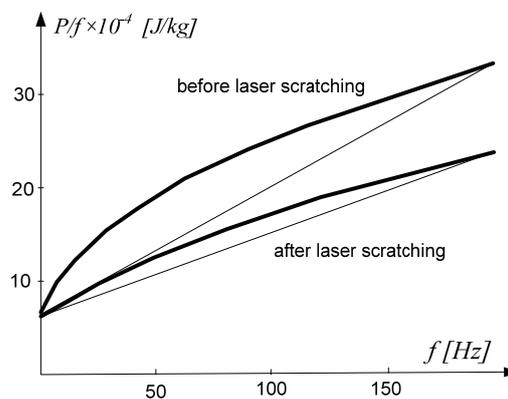


Fig. 17. Core loss per cycle before and after laser scribing (0.23 mm GO 3% SiFe (after [20]))

### SiFe non-oriented electrical steel

As it is presented in Fig. 11 grain oriented SiFe steel is strongly anisotropic what means that in other direction then easy axis (rolling direction) magnetic properties are poor. Thus if we cannot guarantee that direction of magnetic flux is the same as rolling direction (for example in rotating machines) we can obtain bad performances of designed device. In such case the non-oriented material is more advisable.

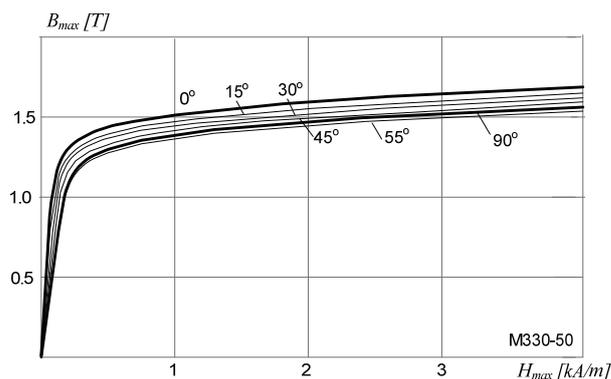


Fig. 18. Magnetization curves of typical non-oriented steel - determined for different angles of magnetization

Fig. 18 presents the magnetization curves of typical NO steel determined for different angles of magnetization. It should be noted that this material is not pure isotropic but in comparison with grain oriented steel the change of properties with the change of direction of magnetization are acceptable small. That is why NO material is much more often used than grain oriented.

Fig. 19 presents collection of the main properties of typical nonoriented SiFe steel. For comparison on the same picture are presented the same properties of CGO (conventional grain oriented) steel. We see that generally NO steel is a worse quality in comparison with CGO. But in many devices such poor properties are acceptable mainly taking into account economic point of view - NO steel is much cheaper. Moreover because this SiFe steel contains less silicon (0 - 3 %) it is more ductile what means that more devices we can punch with the same stamping device.

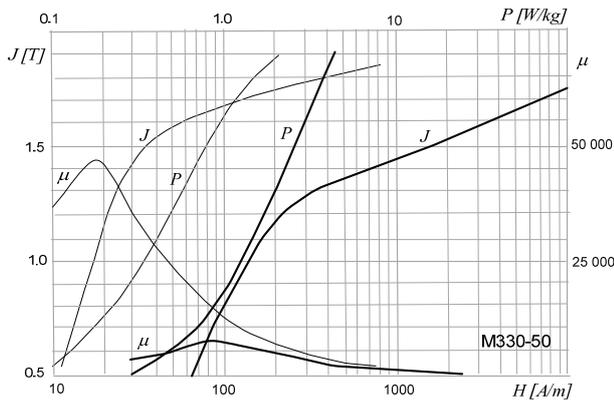


Fig. 19. Properties of typical NO steel (thin line - the same properties of typical grain-oriented steel for comparison)

NO steel is delivered in two possible forms - fully finished or semi-finished. In the case of semi-finished steel the customer have to anneal the material after stamping. Semi-finished steel is in only a partly decarburised to obtain better punchability (final decarburisation is obtain in final annealing). Because it is not necessary to perform 24 hours annealing for recrystallization and grain growth the production process is much simpler (and cheaper).

During annealing care should be taken to not allowed to extra grain growth. Therefore time of annealing and time of cooling should be precisely controlled. The optimal grain size is around 100 - 200  $\mu\text{m}$  (Fig. 20).

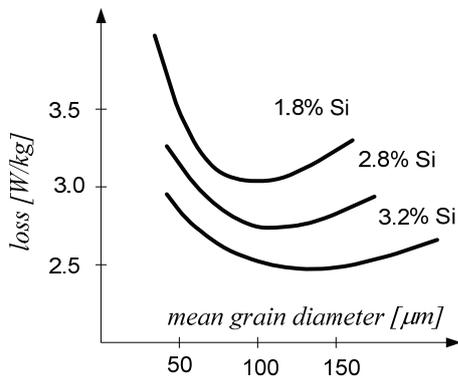


Fig. 20. Influence of mean grain diameter on loss (after [21])

As a hysteresis loss is almost 75% of total loss in NO SiFe presence of impurities directly related to this loss is a crucial for NO steel quality. Therefore so important is the starting material and technology of remove carbon (decarburization), oxide, sulphur and nitride. In modern NO steel these doses are below 10 ppm. NO SiFe steel is manufactured with different contents of silicon. Table 3 presents the properties of NO electrical steel of various contents of Si.

No SiFe steel is usually delivered in coated form. Various coating materials, organic or inorganic are used. Coating plays important role because it is not only the insulating layer, but also save against oxidation, should ensure good punchability, in certain cases it can intriduce stress to improve quality. Comprehensive review on this subject presents review article of Coombs [22].

Table 3. Classification of NO SiFe steel [23]

	% Si	thickness [mm]	loss <sub>1.5</sub> [W/kg]
Top grades	2.5 - 3.2	0.35 - 0.5	2.2 - 2.5
Medium grades	1.5 - 2.5	0.35 - 0.5	4 - 6
Low grades	0.5 - 1.5	0.5 - 0.65	7 - 9
Non-Si		0.65 - 1	8 - 12

### Unconventional iron based alloys

From data presented in Fig. 7 results that by enlarging the contents of Si in the SiFe steel we can obtain attractive material in comparison with 3% SiFe. Although saturation polarization decreases with silicon contents the *nonmagnetostrictive 6.5% SiFe* exhibits almost two-times larger resistivity what made it a good candidate for medium frequency applications (due to significantly smaller eddy current losses). Moreover *6.5% SiFe* is has very small magnetostriction.

The main problem is that this material is hard and brittle and it is not possible to prepare it by conventionally cold rolling. Therefore several other manufacturing technologies of this material are proposed: by powder rolling processing , by rapid solidification or chemical vapor deposition (CVD).

The rapid solidification technology is used to avoid formation of FeSi (B<sub>2</sub>) and Fe<sub>3</sub>Si (DO<sub>3</sub>) phases because they make the material brittle. The molten metal stream is ejected onto a rotating metallic drum. As result is obtained thin (30 - 100  $\mu\text{m}$ ) ribbon with acceptable ductibility, coercivity lower than 10 A/m and maximum permeability larger than 10 000. The average grain diameter is 5 - 10  $\mu\text{m}$  therefore sometimes this materials is called as *microcrystalline material*. The main advantage of microcrystalline 6.5 % SiFe is much more wider frequency bandwidth in comparison with conventional SiFe (Fig. 21). From Fig. 21 results that 6.5% SiFe is superior in comparison with 3.2 % SiFe above around 100 Hz.

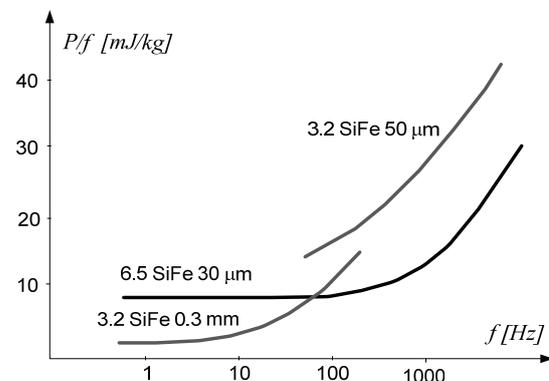


Fig. 21. Core loss per cycle of microcrystalline 6.5 SiFe (and comparison with conventional 3.2 % SiFe) (after [24])

Convenient for large volume manufacturing is technology CVD (chemical vapor deposition). In this technology conventional 3% SiFe is chemically polished and next is held at 1000 °C for 1 hour under a flowing gaseous mixture of SiCl<sub>4</sub> and argon (Fig. 22). Near the surface of the sheet is formed Fe<sub>3</sub>Si and the sheet loss Fe as a gaseous FeCl<sub>2</sub>. Next 13 hours diffusion process at 1000 °C led to a homogeneous FeSi solution. In this way it is possible to obtain various thickness grain-oriented or nonoriented 6.5 % SiFe sheet.

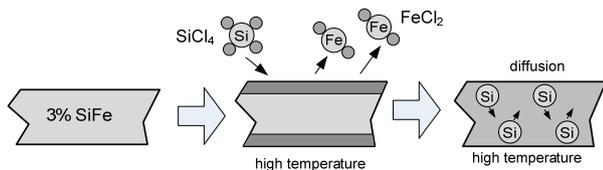


Fig. 22. CVD technology of 6.5% SiFe production (after [24])

As result of CVD siliconization it is observed significant improvement most of all frequency properties. Fig. 23 presents the change of energy loss after CVD process.

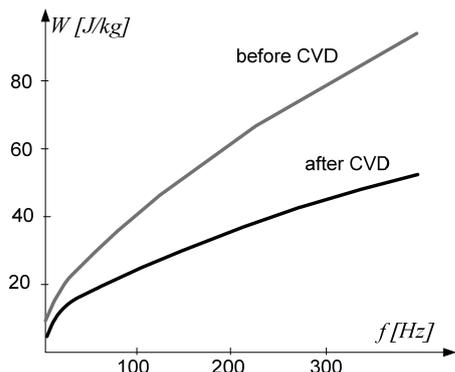


Fig. 23. Energy loss versus frequency of 6.5 SiFe

Since 1993 NKK Corporation started with the commercial scale production of 6.5% SiFe by CVD siliconizing process. Several grades of 6.5 SiFe called NK E-core 0.05, 0.1, 0.2 and 0.3 mm thick was market available. Table 4 presents performances of NKK 6.5 SiFe. For medium frequency this material is much better than conventional steel and can be an alternative for amorphous material.

Table 4. Properties of 6.5% SiFe (NKK E-core) (after [24]) and comparison with other materials

	T [mm]	J <sub>s</sub> [T]	Loss [W/kg]				
			1T 50 Hz	1T 400	0.5T 1k	0.2 T 5k	0.1 T 10k
NK E-core 6.5%	0.05	1.25	0.85	7.0	5.2	8.0	5.1
	0.1	1.25	0.72	7.3	6.2	11.8	9.7
	0.2	1.27	0.55	8.1	8.4	19.0	16.8
	0.3	1.30	0.53	10.0	11.0	25.5	24.5
3% SiFe	0.05	1.79	0.68	7.2	7.6	19.5	18.0
	0.1	1.85	0.72	7.2	7.6	19.5	18.0
	0.23	1.92	0.29	7.8	10.4	33.0	30.0
	0.35	1.93	0.40	12.3	15.2	49.0	46.0
amorph Fe-Si-B	0.03	1.38	0.13	1.5	2.2	4.0	4.0

From time to time returns the idea of cubic texture. Indeed looking at Goss texture (Fig. 24) the position of crystal seems to be rather extravagant. More natural order, like cobbles seems to be cube order. Moreover in the Goss texture is one easy direction and perpendicular to it hard direction - in cube texture both directions are easy. It could be profitable in rotating machines.

First information about possibility to obtain SiFe electrical steel with cube texture published Sixtus in 1935 [25]. In 1957 Assmus describe condition of processing and annealing necessary to have cubic orientation. By applying this technology Kohler confirmed this technology by

applying annealing of 3% SiFe in slightly oxidizing atmosphere.

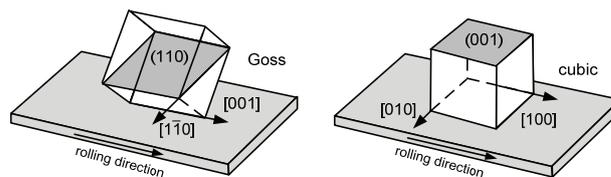


Fig. 24. Goss (110)[001] and cubic (001)[100] texture

From that time other technological possibilities were demonstrated - for example by rolling the sheet two times in perpendicular directions. In 1988 was published patent describing technology where starting point to cubic texture was {114} <401> texture [26]. In the seventies two manufacturers Armco Steel and Vacuumschmelze offered in laboratory scale electrical steel with cubic texture.

But such material did not accepted by the market. Cubic SiFe steel was expensive (due to much complex technology of producing), with large magnetostriction and therefore also recently it is probably prepared in only laboratory scale.

Other alternative to SiFe steel is iron - aluminum alloy. Aluminum changes the resistivity in similar way like silicon. Indeed 16% Al-Fe exhibits large resistivity  $\rho = 140 \mu\Omega\text{m}$ , almost four times larger than 3% SiFe. Additionally it exhibits reasonable small coercivity and large permeability (after annealing it can be around 50 000). The drawback of AlFe steel is that this material is more susceptible to oxidation.

On the market is present 16% Al-Fe known as *alperm* (also as *alfenol*). Due to large resistivity it can be used for medium frequency applications [Adams 1962]. Another alloy - 13% Al-Fe known as *alfer* exhibits large magnetostriction what is applied in sensors.

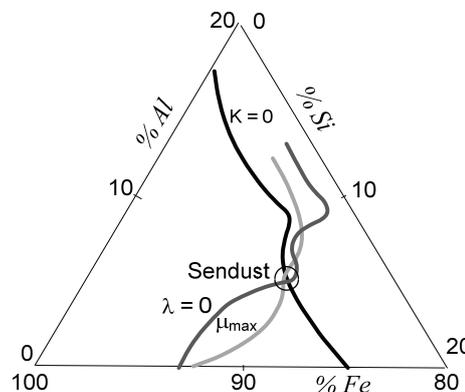


Fig. 25. Parameters of FeAlSi alloy

In 1936 Masumoto developed new Fe-Si Al alloy known as *sendust*. This alloy (84.9 Fe - 9.5 Si - 5.6 Al) has very large permeability (even 140 000), low coercivity and large resistivity [27]. Additionally it exhibits unique feature - simultaneous zero magnetostriction and zero magnetocrystalline anisotropy constant  $K_1$ . It can be used in medium or high frequency applications as competitive to NiFe alloys. Due to its hardness it was used as reading head. Because it is very brittle often it is manufactured as powder core. Table 5 present performances of main iron - aluminum alloys.

Table 5. Properties of Al-Fe alloys (after [28])

		$J_s$ [T]	$H_c$ [A/m]	$\mu_{max}$
Alfer	13% Al	1.28	53	4 000
Alperm	16% Al	0.8	3	55 000
Sendust	10% Si, 5% Al	1	4	140 000

**Nickel and cobalt based alloys**

**NiFe alloys (Permalloy)**

Permalloy<sup>2</sup> (FeNi alloys) many years was the symbol of the highest quality soft magnetic materials - with extremely high permeability ( $\mu_{max} = 1\ 000\ 000$  in the case of Supermalloy) and small coercivity ( $H_c = 0.2$  A/m in the case of Supermalloy). Superiority of Permalloy illustrates impressive figure 3.34 from Fiorillo book [29]. Recently importance of NiFe alloys is shadowed by new stars: amorphous and nanocrystalline materials having similar or better properties.

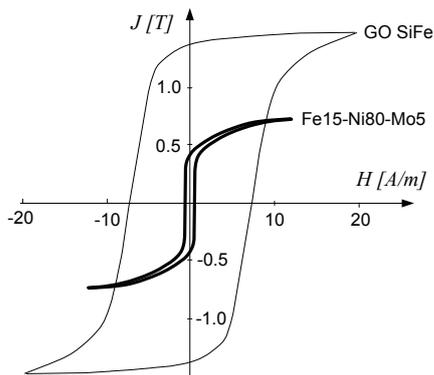


Fig. 26. Comparison of the hysteresis curve of NiFe and FeSi alloys (after [29])

By appropriate selection the alloy composition (supported by third element as Mn, Cu, Cr, V) and annealing/cooling treatment it is possible to obtain the alloy exhibiting various, often extraordinary properties, as for example:

- alloy with close to zero coefficient of thermal expansion (FeNi36 known as *invar* or Fe59Ni36Cr5 known as *elinvar*);
- alloy of the coefficient of thermal expansion the same as glass (Fe53.5Ni29Co17Mn0.3Si0.2 known as *kovar*);
- alloy with very large permeability (Fe16Ni79Mn4 known as *supermalloy* or Fe16Ni77Cu14 known as *mumetal*);
- alloy with constant permeability (Fe55Ni36Cu9 known as *isoperm*);
- alloy with permeability linear dependent on temperature (Fe70Ni30 known as *thermoperm* or Ni67Fe2Cu30 known as *thermalloy*);
- alloy of square hysteresis loop (Fe50Ni50 known as *hipernik* or *permenorm*).

Flexibility and versatility of FeNi as a function of temperature treatment and composition are advantageous but in some circumstance can be a drawback. FeNi alloys are very changeable in use, after stamping and shocks it is necessary to carefully annealing the material.

Fig. 27 presents dependence of NiFe alloy properties on the nickel contents. There are three main areas of application:

- close to 80% where the permeability is very large and coercivity is small;

- close to 50% where the saturation polarization is the largest;
- close to 36% where resistivity is large.

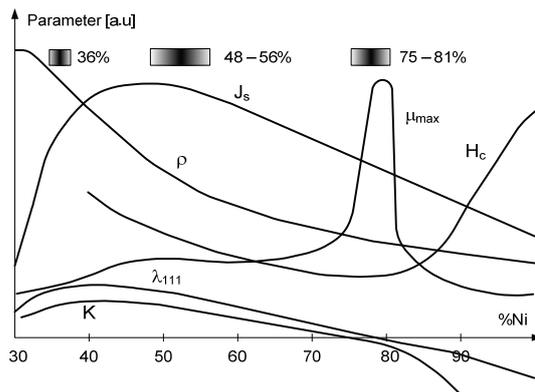


Fig. 27. Dependence of the NiFe alloy parameters on the nickel contents

The anisotropy constant and magnetoelasticity constant are close to zero around 75-91% Ni. Unfortunately it is not possible to obtain zero value of both parameters simultaneously (as for example is possible in Sendust) but with small addition of other components (molybdenum, copper) it is possible to obtain nonmagnetostrictive material with zero anisotropy constant.

Table 6. Properties of NiFe and CoFe alloys

	$J_s$ [T]	$H_c$ [A/m]	$\mu_{max} \times 1000$	
Fe64Ni36	1.3	40	20	invar
Fe50Ni50	1.6	7	15	isoperm
Fe52Ni48	1.6	8	180	
Fe44Ni56	1.5	1	300	
Fe20Ni80	1.1	0.4	100	permalloy
Fe16Ni79Mo5	0.8	0.4	550	supermalloy
Fe16Ni77Cu5Cr2	0.75	0.8	500	mumetal
Fe50Co50	2.45	160	5	permenorm
Fe49Co49V2	2.4	400	17	hiperco,

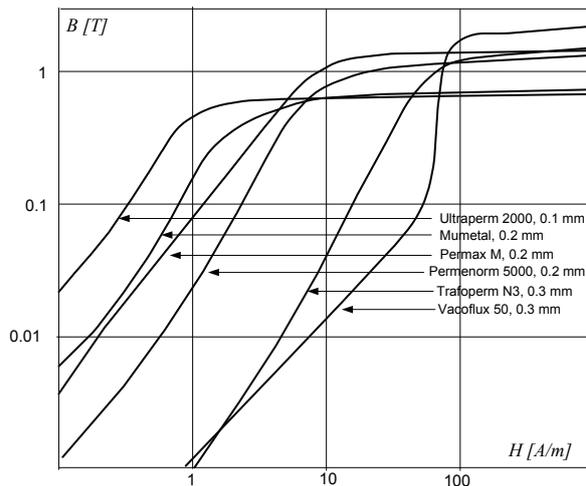


Fig. 28. Magnetization curves of various NiFe and CoFe alloys (Vaccumschmelze data: *ultraperm* and *mumetal* alloys from 72-83% NiFe group, *permax* from 54 - 68 % NiFe group, *permenorm* from 45-50 % NiFe group, *trafoperm* - nearly isotropic SiFe, *vacoflux* - 50% Co alloy)

Table 6 presents the parameters of the main NiFe alloys. In application of NiFe alloys two types of alloys are important. The first is around 80% of Ni with high

<sup>2</sup> Name Permalloy is formally related to only one type of NiFe alloys - the non-magnetostrictive NiFe alloy with Ni contents around 80%. But it is commonly used to all types of NiFe alloys.

permeability, small coercivity and close to zero magnetostriction. These alloys are most of all used as shields (mumetal) and for sensors (supermalloy). To obtain high permeability the special heat treatment called permalloy treatment (or double treatment). This annealing consist of heating for 1 hour at 900 - 950 °C and cooling at the maximum rate of 100 °C/hour to room temperature. Next heating to 600 °C and cooling in the open air to room temperature by placing on the copper plate.

High permeability alloys have small resistivity and small saturation polarization. Therefore for other purposes (as pulse transformers, audiofrequency transformers, null balance transformers, switches, chokes etc) are used alloys around 50% Ni.

NiFe alloys are also available in form of the powder cores known as *MPP* (Molybdenum Permalloy Powder - Ni81Fe17Mo2).

#### CoFe and CoFeNi alloys (Permendur and Perminvar)

Alloys of around 50% Co is known as *permendur* - the alloy of the highest available saturation polarization - up to 2.46 T. Data and characteristics of such alloy have been presented in previous Section (Table 6 and Fig. 28).

To improve the material properties small of vanadium (2%) is added. In this way resistivity and ductile is improved part at the cost of small decrease of saturation polarization. Exist also special kind of permendur alloy with careful control of purity and magnetically annealed known as supermendur. *Supermendur* exhibits much smaller coercivity around 10 A.m and large permeability around 80 000.

CoFe alloys are used in applications where high saturation induction is necessary - for example as poles of electromagnets. As higher flux density as smaller and less heavy electrical machine. That is why this alloy is used in aircraft industry.

Exist also NiFeCo alloys - the most known is *perminvar* Ni45Fe30Co25 - the alloy with constant permeability (invariant permeability) over a wide range of applied field values.

#### Amorphous and nanocrystalline alloys

##### Amorphous soft magnetic materials (metallic glass)

Fig. 29 illustrates technology of producing the amorphous ribbon. The material in the liquid state is rapidly cooled on the rotating cooper drum. The speed of cooling should be fast enough to not allowed to form crystal structure. Therefore to help the formation of amorphous state to the melt id added metalloïd (mostly boron) to improve viscosity. Since the ribbon should be cooled very quickly it is thin with the thickness not exceeding 50 µm. Also the width of the ribbon is limited usually not exceeding 20 cm.

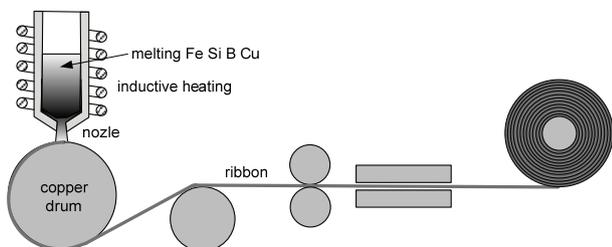


Fig. 29. Technology of producing the amorphous ribbon

Table 7 presents the data of main amorphous ribbons. Exceptional performances exhibit cobalt based alloys - very large permeability, small coercivity, possibility to obtain

material with negligible magnetostriction. But these alloys suffer from small polarization and low Curie temperature. On the other hand iron based alloys exhibits larger polarization but at the cost of permeability and coercivity. The highest polarization is possible to obtain by adding of about 20% of expensive cobalt to iron based alloy. Intermediate properties exhibit FeNi-Mo alloys that make them suitable for shielding purposes.

Table 7. Properties of main amorphous alloys (after [30])

	$J_s$ [T]	$H_c$ [A/m]	$\mu_{max} \times 1000$	$\rho$ [ $\mu\Omega\text{cm}$ ]	$T_c$ [°C]
FeSiBC	1.6	2.2	300	135	370
FeSiBCo	1.8	4	400	123	415
FeNiMoB	0.9	1.2	800	138	350
CoNiFeBSi	0.6	0.3	1 000	142	225

The magnetic parameters of amorphous ribbon can be improved by annealing, especially by annealing in longitudinal magnetic field. Because metallic glass is brittle usually heat treatment is performed on ready toroid. This way are removed stress, also this caused by wound of toroid. The temperature should not exceed crystallization temperature that is around 400 °C for NiFe alloys, 480 for Fe alloys and 550 for Co alloys.

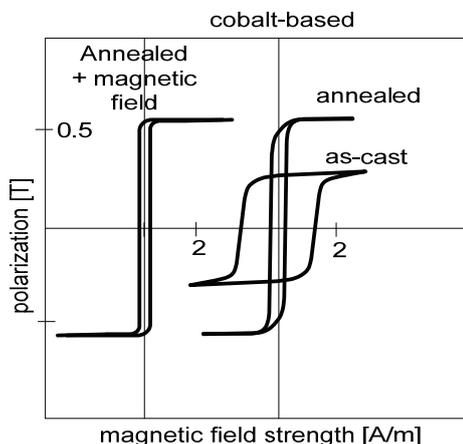


Fig. 30. Effect of annealing of amorphous ribbon (after Metglas Inc. data)

Table 8. Market available amorphous materials

	$J_s$ [T]	$\mu_{max} \times 1000$	$\lambda \times 10^{-6}$
Metglas 2605 SA1	1.56	600	27
Metglas 2605 SC	1.61	300	30
Metglas 2605CO	1.8	400	35
Metglas 2705 M	0.77	800	<0.5
Metglas 2714 A	0.57	1000	<0.5
Matglas 2826 MB	0.88	800	12
Vitrovac 6025	0.55	600	0.3
Vitrovac 6030	0.8	300	0.3

The amorphous alloys have been introduced in seventies by Allied Signals Inc. Metglas Products. Recently market available products are offered by Metglas Inc - Hitachi Metals and by Vaccumschmelze. Table 8 presents data of market available soft magnetic amorphous materials. Typical thickness of the ribbon is around 25 µm, width does not exceed 20 cm. The most versatile is Metglas SA1 with relatively large saturation induction, permeability and small; power loss.

Amorphous alloys without any problems can work in high frequency bandwidth. It is the main application of this material, as power transformers, pulse transformers, high frequency transformers, current transformers, ground fault

interrupters. Indeed as it illustrates Fig. 31 amorphous materials are superior to the 1 MHz in comparison with other materials.

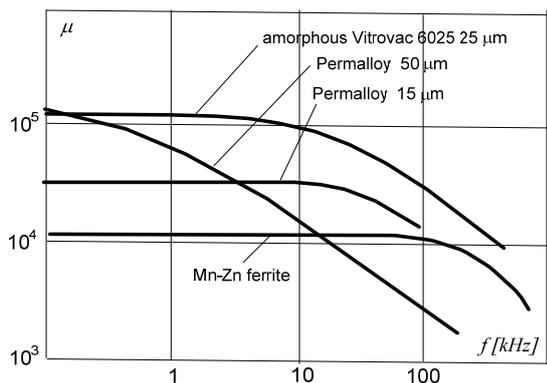


Fig. 31. Permeability versus frequency of different magnetic materials (toroidal cores) (after [31])

Another important application of amorphous materials is profiting of the exceptionally large permeability - in Co-based alloy even 1 000 000. Such large permeability especially is recommended in shielding and sensor application.

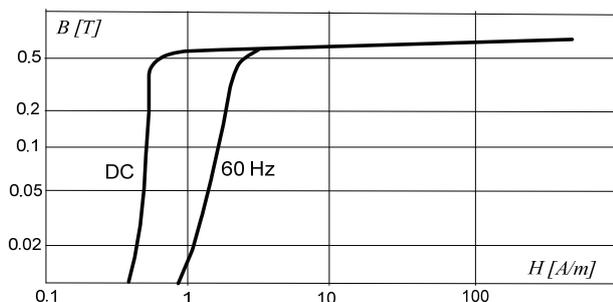


Fig. 32. The magnetization curve of cobalt Metglas 2705M (after Metglas Inc. data)

It is still under discuss possibility to apply the amorphous core in power transformers [Moses 1994, Hasegawa *et al* 2008]. Indeed comparison of power loss at 1.3 T - 0.64 W/kg in the case of silicon steel and 0.11 W/kg in the case of amorphous ribbon is impressing.

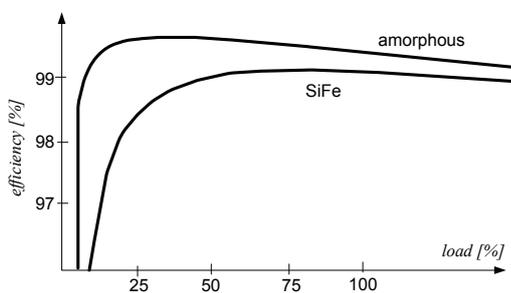


Fig. 33. The efficiency of 2000 kVA dry-type transformer [32]

After introduction of amorphous alloys it was expected that they should substitute conventional distribution transformer due to smaller loss and better efficiency. Up to 1990 about 20 000 AMDT transformers (Amorphous Metal Distribution Transformer) have been installed in USA (in Japan about 32 000 units) [33]. Although amorphous

material has smaller power loss in comparison with GO SiFe steel (due to smaller coercivity and larger resistivity) exist several obstacles in wide expansion of AMDT units.

Amorphous ribbon is very thin (about 25 μm) and narrow (10 - 20 cm) what make difficult design and manufacturing of transformers. Practically only wound cores are applicable. In the case of one-phase distribution (dominant in USA and Japan) design of wound amorphous core transformer is relatively easy. In the case of three-phase distribution (dominant in Europe) the design of AMDT unit is still a challenge.

Table 9. Performances of 3-phase 500 kVA transformer [32]

	SiFe	Metglas SA1
weight (ratio)	1	1.23
No load loss [W]	665	215
40% load loss [W]	1353	1207
Audible noise [dB]	53	58

Very significant obstacle is lower saturation induction 1.56 T for most popular Metglas 2605 SA1 ribbon in comparison with 2.03 for GO SiFe. That is why Metglas Inc. introduced new grade Metglas 2605 HB1 with improved properties:  $B_s = 1.64$  T and  $H_c = 2.4$  A/m (in the case of Metglas 2605 SA1  $H_c = 3.4$  A/m) [Hasegawa 2006]. Table 9 presents performance of a 50 Hz 3-phase 500 kVA transformer, and Fig. 33 presents the efficiency of distribution transformer.

It was estimated that in USA for annual transformer loss around 140 TWh introduction of AMDT transformers results in saving of around 80 TWh what corresponds with 60 tone of CO<sub>2</sub> annual reduction [Hasegawa 2008]. In 2009 ABB Corp. announced starting of production of AMDT transformers in New Jersey.

#### Nanocrystalline materials

In 1988 Yoshizawa and co-worker from Hitachi Metals Company proved that after appropriate annealing of Fe-based amorphous ribbon it is possible to create very small grains of α-FeSi (diameter around 10 nm) embedded in amorphous matrix (Fig. 34) [34].

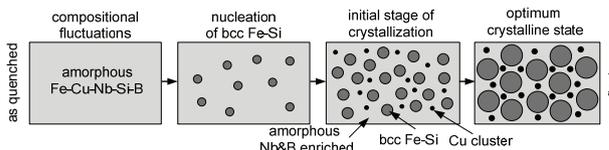


Fig. 34. Formation of nanocrystalline structure during controlled annealing [35]

This new material called FINEMET exhibited excellent magnetic properties, close to those possible to obtain in Co-based, much more expensive amorphous ribbon. As the initial amorphous material Fe<sub>73.5</sub>Cu<sub>1</sub>Nb<sub>3</sub>Si<sub>13.5</sub>B<sub>9</sub> ribbon with thickness 20μm was used (note that also expensive boron was used in smaller amount than in the typical amorphous material). Copper was added to enhance the nucleation of α-Fe grains and niobium was used to lower the growth of the grains. The temperature of annealing for about one hour was above the crystallization temperature - around 550 °C. Moreover as starting material had saturation magnetostriction  $\lambda_s = 20 \cdot 10^{-6}$  after annealing the nanocrystalline material exhibited close to zero magnetostriction. Thus the paper of Yoshizawa was the start point for the new class of soft magnetic material known as a nanocrystalline material. Fig. 35 shows the performances of material presented in paper of Yoshizawa.

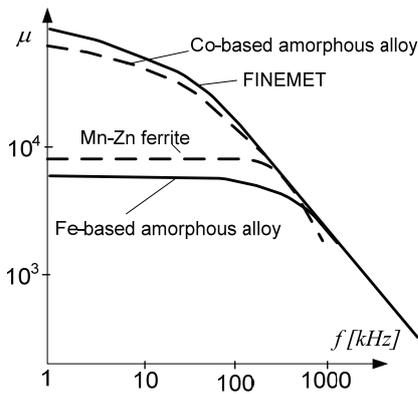


Fig. 35. Properties of the FINEMET material (after [34])

After information about FINEMET material many other information about similar or other nanocrystalline were published. The most wide known are NANOPERM and HITPERM. Team from Tohoku University in 1981 proposed to substitute Nb by other transition metal as zirconium Zr or hafnium Hf [36]. Typical materials as  $Fe_{87}Zr_7B_5Cu_1$  or  $Fe_{86}Zr_7B_6Cu_1$  are known as NANOPERM. Such materials have been obtained by rapid solidification of melting mixtures or by compaction of the powder using hot-pressing machine [37].

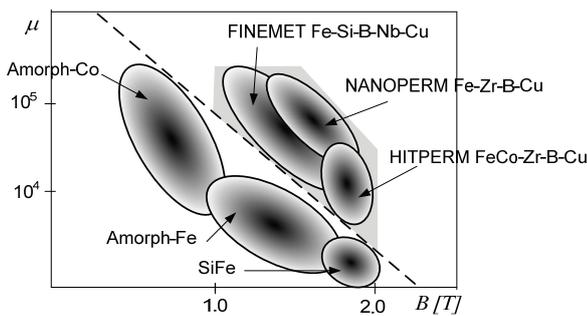


Fig. 36. Permeability and polarization range of main nanocrystalline materials

The FeCo nanocrystalline alloys with composition (FeCo)-M-B-Cu (where M - Zr, Hf, Nb, etc) enable to obtain saturation polarization close to polarization of SiFe [Villard *et al* 1999, 1999a]. These alloys are known as HITPERM. They can work correctly in elevated temperatures up to 650 °C. Table 10 presents the main features of nanocrystalline alloys.

Table. 10. Properties of the main nanocrystalline alloys [35]

	$J_s$ [T]	$H_c$ [A/m]	$\mu$ (1 kHz)	D [nm]
$Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$	1.24	0.5	100 000	13
$Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$	1.23	0.4	110 000	14
$Fe_{84}Nb_7B_9$	1.49	8	22 000	9
$Fe_{86}Cu_1Zr_7B_6$	1.52	3.2	48 000	10
$Fe_{91}Zr_7B_3$	1.63	5.6	22 000	17
$Fe_{67}Co_{18}Si_1B_{14}$	1.8	5	1 500	

The most commonly used nanocrystalline material is close to  $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$  alloy and is available under different trade names: Finemet, Vitroperm, Nanophy.

Usually nanocrystalline material is delivered as ready to use toroid, for example choke or transformer because nanocrystalline material is very sensitive to annealing conditions. Not correct temperature of annealing leads to significant increase of coercivity due to growth of grain diameter (coercivity depends on grain diameter as  $D^6$ ).

Similarly small changes of alloy composition cause significant changes of parameters.

### Soft ferrites

Ferrites are the ceramic ferrimagnetic materials in the structure of spinel. Investigating various possible composition of ferrites Snoek predicted that two main class of materials MnZn and NiZn ferrites should exhibit the best performances [38]. And indeed although investigated are various soft ferrites compositions [Stoppels 1996] on the market are available these two main families of material. They are complement each other. Table 11 presents the main properties of both class of soft ferrites. MnZn ferrites exhibit higher permeability and saturation polarization but NiZn ferrites have much larger resistivity (close to insulation) and therefore can be used for higher frequencies (1 MHz - 500 MHz while MnZn up to several MHz).

Table 11. Properties of MnZn and NiZn ferrites [39]

	$\mu_{in}$	$J_s$ [T]	$H_c$ [A/m]	$\rho$ [ $\Omega m$ ]	f [MHz]
MnZn	500-20 000	0.3-0.5	4-100	0.02-20	DC - 1
NiZn	10-2000	0.1-0.4	16-1600	$10^{-10}$	1 - 500

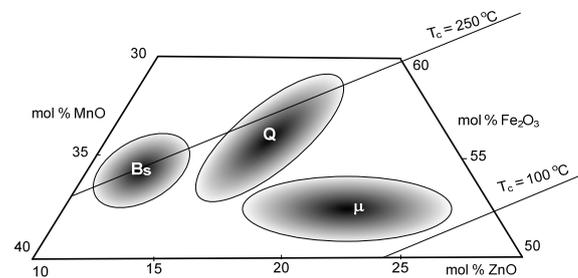


Fig. 37. Phase diagram of MnO-ZnO-Fe<sub>2</sub>O<sub>3</sub> (from Ferrite Users Guide edited by Magnetic Materials Producers Association MPPA)

Both class of ferrites can be described by formulas:  $Mn_xZn_{(1-x)}Fe_2O_4$  or  $Ni_xZn_{(1-x)}Fe_2O_4$ . By changing the composition it is possible to influence the properties of ferrite (Fig. 37). There are three main groups of ferrites: with optimized permeability (for EMI filters, chokes and shield), with optimized saturation polarization (for signal processing) and with optimized loss (quality factor Q) for power application. Generally magnetic properties of soft ferrites are poor in comparison with those of SiFe and additionally these parameters strongly depends on temperature. But on the market there are huge number of various ferrite products due their exceptionally features in high frequency range. Ordinary ferrites of relative low price are also used in many applications where requirements are not excessive.

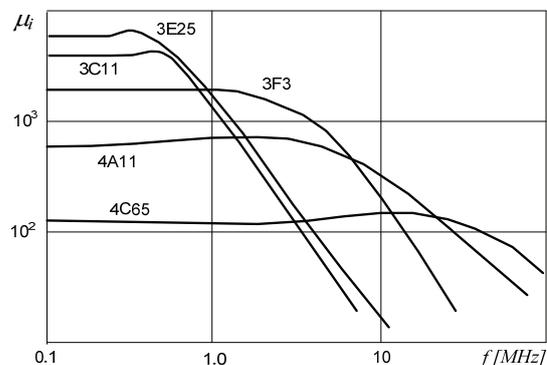


Fig. 38. Diversity of market available ferrites (3 means MnZn ferrites while 4 are NiZn) (from data of Ferroxcube)

Table 12. Properties of typical power ferrites (after [40])

	3C90	3F3	3F4	4F1
type	MnZn	MnZn	MnZn	NiZn
frequency range	25-200 kHz	0.1-7 MHz	0.5-3 MHz	2-20 MHz
$\rho$ [ $\Omega\text{m}$ ] 25° DC	5	7	10	$2 \cdot 10^5$
$\rho$ [ $\Omega\text{m}$ ] 100° DC	1.3	2	3	$3 \cdot 10^4$
$\rho$ 25° 100kHz	4	6	7	$1 \cdot 10^5$
$\rho$ 25° 1MHz	1	1.5	3	$5 \cdot 10^4$
$\rho$ 25° 10MHz			0.6	$2 \cdot 10^4$
av. grain size $\mu\text{m}$	7	5	2	3
$\mu$ 10kHz, 0.1 mT	2 000	1 800	800	80
$B_s$ [T]	0.5	0.5	0.44	0.32
loss P [mW/cm <sup>3</sup> ]				
25 kHz 200 mT	60	100		
100 kHz, 100 mT	70	70		
500 kHz 50 mT		200	180	
1 MHz 30 mT		390	150	
3 MHz 10 mT			220	150
5 MHz 10 mT				300
10 MHz 5 mT				150

Modern electronic devices are working at more and more higher frequencies. Therefore there is a need of magnetic materials for GHz range, up to 150 GHz. In many microwave devices magnetic part is very important, taking into account antennas, circulators, isolators, phase shifters, filters. Fortunately exist ferrites working in microwave range.

In microwave range three most important materials can be use: garnets ferrite (in the range 1 - 10 GHz), spinel ferrites (in the range 3 - 30 GHz) and hexagonal ferrites (in the range 1 - 100 GHz).

**Hard magnetic materials**

In the case of soft magnetic materials we require coercivity as small as possible because hysteresis power loss strongly depends on this value. Reversely in the case of hard magnetic materials we needs to have as large as possible coercivity and remanence because stored magnetic energy approximately depends on the  $H_c \cdot B_r$  value. Possible to obtain magnetic field of the magnet directly depends on the (BH) value - called often as an energy product.

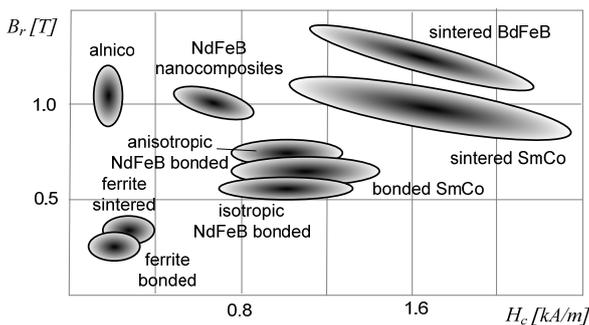


Fig. 39. Comparison of the main hard magnetic materials [41]

Table 13. Properties of the main hard magnetic materials

	$(BH)_{max}$ [kJ/m <sup>3</sup> ]	$jH_c$ [kA/m]	$B_r$ [T]	$T_c$ [°C]	Price (relative)
FeCoCr	7	20	0.9		-
Ferrite	28	275	0.4	450	1
Alnico	40	124	1.2	850	10
NdFeB	320	1200	1.0	310	20
SmCo	160	1500	0.95	720	100

Performances of the magnet strongly depend on the demagnetization factor  $B/\mu_0 H$  therefore on the on the B(H) dependence (left quadrant) are usually indicated lines representing  $B/\mu_0 H$  as well curves representing BH values (Fig. 40). This way the designer of the magnet can at once determine possible performances of the material and recommended geometry of the magnet.

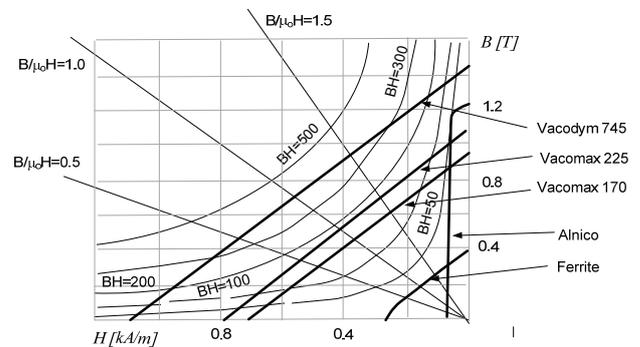


Fig. 40. The demagnetizing curves of various materials (from Vacuumschmelze catalogue)

**Alnico alloys**

Alnico was discovered in 1930 by Mishima and the first classical alloy contain 58% Fe, 30% Ni and 12% Al. It exhibited coercivity of over 30 kA/m what was almost double that the best steel magnets. Till introduction of the rare earth magnets in 1970s alnico was the main hard magnetic material. Recently its importance is smaller (see Fig. 3.61) - its main advantage is still high working temperature - up to 500 °C. Alnico was evaluated to other composition (addition of cobalt and titanium) known as Alnico2, Alnico3, ..., Alnico 9 (Fig. 41).

Various types of alnico differ not only by the composition but also by heat treatment (including annealing in magnetic field) - they are isotropic or anisotropic, non-oriented and grain oriented. The performances of alnico alloys are presented in Table 14.

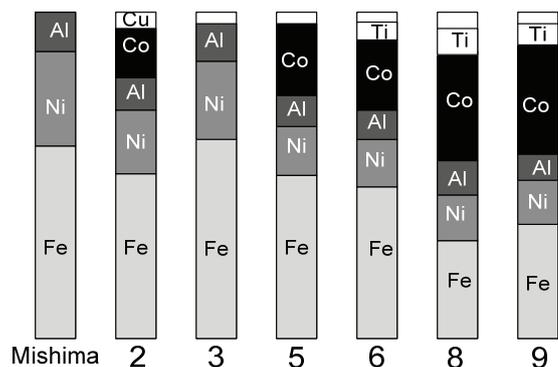


Fig. 41. Various compositions of alnico alloys.

Table 14. Properties of alnico alloys (from Arnold Magnetic Technologies)

	$B_r$ [T]	$B H_c$ [kJ/m <sup>3</sup> ]	$(BH)_{max}$ [kJ/m <sup>3</sup> ]	
Alnico 2	0.72	45	12.7	Isotropic 12-20% Co
Alnico 3	0.7	38	11.1	Isotropic, Co-free
Alnico 4	0.55	57	10.7	isotropic
Alnico 5	1.32	240	51.7	anisotropic, oriented
Alnico 6	1.08	240	31	anisotropic, titanium
Alnico 8	0.93	480	47.7	anisotropic, high $H_c$
Alnico 9	1.12	480	83.6	columnar, oriented

Alnico are recognized as Alnico2, ..., Alnico 9 or by trade names: Alni, Alcomax, Hycomax, Ticonal. In manufacturing of alnico alloy very important is heat treatment, often in presence of magnetic field. After heat treatment alnico transforms to a composite material with rich iron and cobalt precipitate in rich-NiAl matrix. Starting from Alnico 5 anisotropy is improved due to grain orientation - after heating in presence of magnetic field and appropriate cooling the Fe - Co particles are long and ordered in one direction. Starting from Alnico 6 to the alloy is added titanium that increases the coercivity. In Alnico 9 after appropriate heat treatment is obtain columnar crystallization.

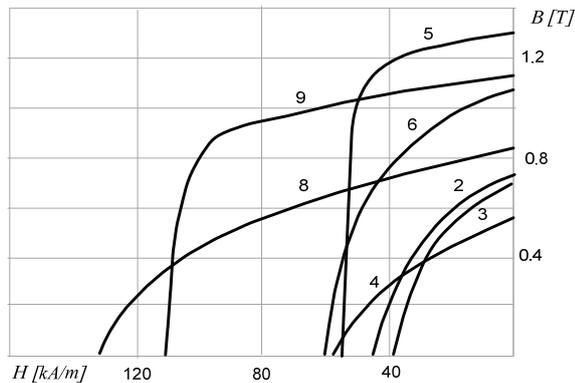


Fig. 42. The demagnetizing curves of different grades of alnico alloy (from Arnold Magnetic Technologies catalogue)

#### Hard magnetic ferrites

Hard ferrites exhibit rather modest performances, especially small saturation. But because are not very expensive they are commonly used in not very demanding applications. Hard ferrites are prepared as sintered from the powder but also composite, bonded materials are available. They are bonding with rubber, PVC, polyethylene or polyester resins. Although bonded materials are inferior in comparison with sintered (as result of reduction of magnetic part in the whole volume) they are popular due to flexibility and low price.

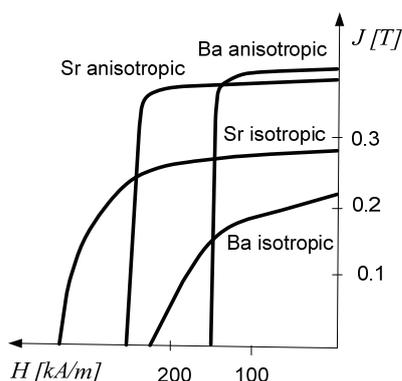


Fig. 43. The demagnetizing curves of different hard ferrites (from [39])

As hard magnetic ferrites almost exclusively two types are manufactured: barium ferrite  $\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$  and strontium ferrite  $\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$ . Both groups of hard ferrites have similar properties although strontium ferrites have slightly better coercivity and saturation. The properties of these ferrites are presented in 43 and Table 15.

Table 15. Properties of typical hard ferrites (from [39])

	$B_r$ [T]	$\mu H_c$ [kA/m]	$J H_c$ [kJ/m <sup>3</sup> ]	$(BH)_{\max}$ [kJ/m <sup>3</sup> ]
$\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$				
sintered, isotropic	0.21	145	240	7.4
sintered, anisotropic	0.4	160	165	29.5
bonded isotropic	0.12	88	190	2.8
$\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$				
sintered, anisotropic	0.38	280	320	26.8
bonded	0.27	196	260	14.0

Exceptional hard magnetic features barium and strontium ferrites have due to two main reasons - they have very large anisotropy and of the powder grain is small (diameter around 1  $\mu\text{m}$ ) every grain is close to one-domain structure. The one domain sample is magnetized by coherent rotation of magnetization and according to Stoner-Wohlfarth model has rectangle hysteresis loop.

The manufacturing process of hard ferrites include calcination in a furnace at about 1200  $^\circ\text{C}$ , formation of the powder, then pressing and sintering at about 1200  $^\circ\text{C}$ . The anisotropic properties are obtained by pressing the powder in presence of magnetic field.

#### Rare earth hard magnetic materials

As for properties of hard magnetic materials crucial is high anisotropy many researchers looked for materials with exceptionally large magnetocrystalline anisotropy. In 1966 Hoffer and Strnat announced that obtained material based on yttrium with very large anisotropy  $K_1 = 5.7 \text{ MJ/m}^3$ . Next other compositions rare earth metal - ferromagnetic mela as Co or Fe have been investigate. The most widely investigated materials have structure:  $\text{RECo}_5$ ,  $\text{RECo}_{17}$ ,  $\text{REFe}_{14}\text{B}$ . As most pronouncing were found light lanthanides. Indeed these elements crystallized in complex hexagonal or rhombohedral structures exhibited not only high anisotropy, but also large saturation polarization

Particularly interest are  $\text{SmCo}_5$  with exceptionally large anisotropy,  $\text{Nd}_2\text{Fe}_{14}\text{B}$  with large saturation and  $\text{Sm}_2\text{Co}_{17}$  with large Curie temperature. Indeed in 1967 first rare earth permanent magnet material  $\text{SmCo}_5$  was proposed as exhibiting the best properties and new era in magnet technology started [42].

Rare earth based materials are prepared similar to the ferrite materials - the powder material with small particles (diameter to several  $\mu\text{m}$  - to obtain conditions close to one-domain) is pressed (sometimes in presence of magnetic field), next sintered at about 1150  $^\circ\text{C}$  for 3 hours. Sometimes this material is next heat treated at temperature 850 - 900  $^\circ\text{C}$ . There are also prepared bonded materials with polymer of epoxy resin.

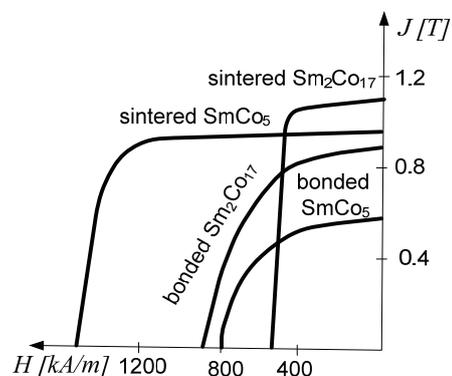


Fig. 44. Typical demagnetizing characteristics of samarium-cobalt materials (from [3])

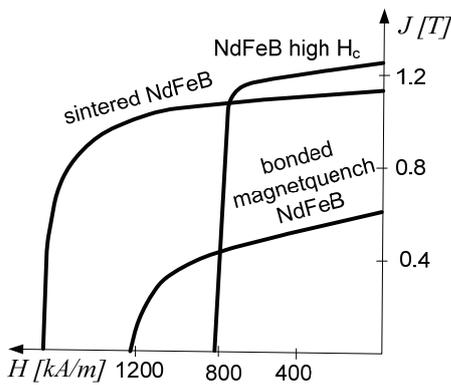


Fig. 45. Typical demagnetizing characteristics of neodymium-iron-boron materials (from [3])

Both components of  $\text{SmCo}_5$  material are expensive. Therefore other similar materials have been tested. One of them is  $\text{MMCo}_5$  or  $\text{Sm}_{0.2}\text{MM}_{0.8}\text{Co}_5$  where samarium is substituted by *mischmetal* MM composed from various other lanthanide, for example 55%Ce, 24%La, 16Nd, 5%Pr and 2% other lanthanide metal.

In other material known as  $\text{Sm}_2\text{Co}_{17}$  it is less cobalt and samarium and are added other components (for example Fe, Mn, Cu, Cr) for improvement the magnetic properties. Fig. 44 presents typical demagnetizing characteristics of samarium-cobalt materials.

In 1984 two teams reported obtaining of new hard magnetic material based on neodymium [43,44]. The new material have much larger saturation polarization, larger coercivity and therefore larger energy product  $(BH)_{\max}$  (Fig. 45). Moreover the new material used less expensive components. That is why recently neodymium magnets moved slightly into shadow samarium based materials.

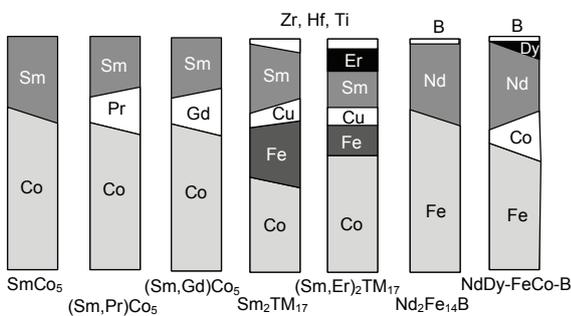


Fig. 46. Various compositions of rare earth hard magnetic materials (after [45])

First reported neodymium materials have been obtained using classical technique (sintering) [43] but also other - by rapid solidification (similar to the technology used in amorphous alloys) [44]. Rapid solidification enables to obtain small grains - about 30 nm while in sintered materials around 3  $\mu\text{m}$ . Theoretically [46] small grains should result in higher coercivity - do date nano-materials and nano-composites exhibit worse parameters than sintered materials.

In other technology known as magnetquench the alloy is rapidly quenched. After grinding the flakes are bonded into an epoxy resin.

Table 16. Properties of typical rare earth hard magnetic materials (after [39])

	$B_r$ [T]	$\delta H_c$ [kA/m]	$J H_c$ [kJ/m <sup>3</sup> ]	$(BH)_{\max}$ [kJ/m <sup>3</sup> ]
$\text{SmCo}_5$	1.00	790	1500	196
$\text{MMCo}_5$	0.80	620	700	124
$\text{Sm}_{0.4}\text{Pr}_{0.6}\text{Co}_5$	1.03	800	1300	208
$\text{Sm}_2(\text{Co}_{0.8}\text{Fe}_{0.14}\text{Mn}_{0.04}\text{Cr}_{0.02})_{17}$	1.13	880	1000	248
$\text{Sm}_2\text{TM}_{17}$ (bonded)	0.89	540	1200	136
NdFeB sintered	1.22	840	1280	280
NdFeB magnetquench	1.17	840	1040	256
$\text{Sm}_2\text{Fe}_{17}\text{N}_3$	1.22	750	2400	160
NdFeB nano (30nm)	1.12		440	157
Vacodym (Vacuumschmelze)	1.47	875	915	415
Vacomax (Vacuumschmelze)	1.12	640	730	240

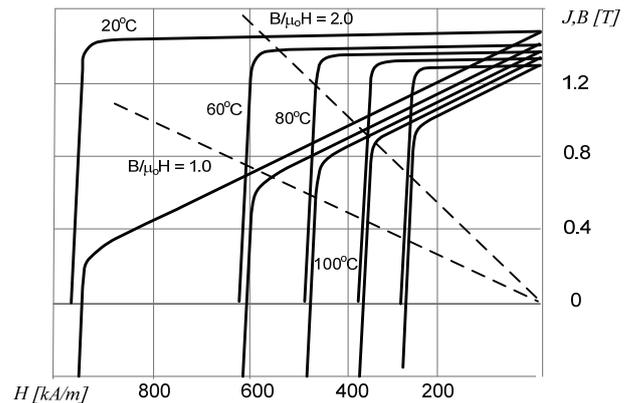


Fig. 47. The demagnetizing characteristics of VACODYM 722 HR hard magnetic material (from Vacuumschmelze catalogue)

Table 16 presents properties of typical rare earth hard magnetic materials. The best performances exhibit sintered NdFeB material, but this material has low Curie temperature 312 °C. Therefore samarium based materials with Curie temperature 820 °C are also market available.

Table 16 presents parameters of market available rare earth hard magnetic materials - VACODYM (neodymium base) and VACOMAX (samarium based) - the best grades of Vacuumschmelze. The Vacodym 722 with  $(BH)_{\max}$  equal to 415  $\text{kJ/m}^3$  is close to theoretical limit - 485  $\text{kJ/m}^3$ . Fig. 47 presents characteristics of this material. It is visible that temperature changes of the parameters are significant. These influence we can diminish by changing geometry of the magnet - compare movement with temperature of the working point for  $B/\mu_0H = 1.0$  and  $B/\mu_0H = 2.0$ .

Based on the Ch.4 of the book "Principles of Magnetic Measurements" (in preparation).

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