

AMORPHOUS AND NANOCRYSTALLINE MATERIALS FOR APPLICATIONS AS HARD AND SOFT MAGNETS

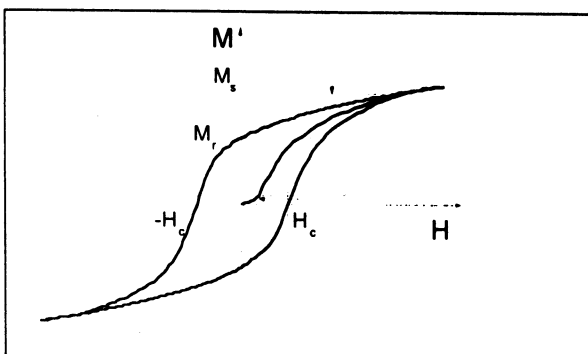
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INTRODUCTION

In the last years great effort was made to improve the magnetic properties of hard and soft magnetic materials. Permanent magnets based on Nd-Fe-B with an energy product of 451 kJ/m³ were recently reported. Any significant further improvement needs a new compound with a higher saturation magnetization.

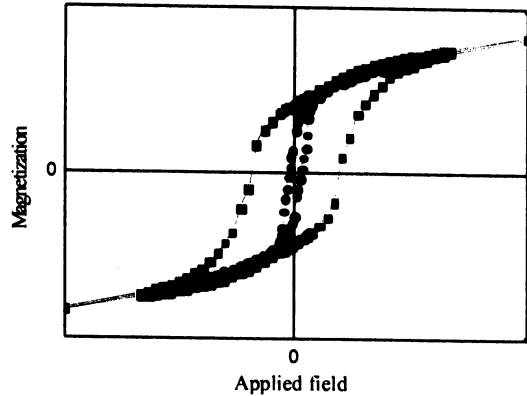
Similar is the situation for soft magnetic materials. There since long time Fe-Si (about 3% Si) was and is the most important material. New developments lead to soft magnetic amorphous materials were the best magnetic properties were found in the system (Fe,Co)₈₀(Metalloid = Si,B)₂₀. Even extrinsic properties such as the permeability, the coercivity and the losses were improved, never a real large scale breakthrough was achieved because of the limited saturation magnetization of about 1.4 T.

This limits were overcome in the last year by the invention of nanocrystalline materials. In this case a special sample preparation procedure leads to nanocrystals (grain size typical 10-30 nm) which exhibited new unexpected magnetic properties. The most outstanding improvement was the remanence enhancement of isotropic hard magnetic materials on one side and also the extremely improved soft magnetic properties on the other side.



Magnetic hysteresis: an important technique for the magnetic characterization

	Soft magnetic material	Hard magnetic material
Coercive force	Low	High (higher than 80 kA/m)
Permeability	High	Not important
Energy density	low	High (B.H) _{max}



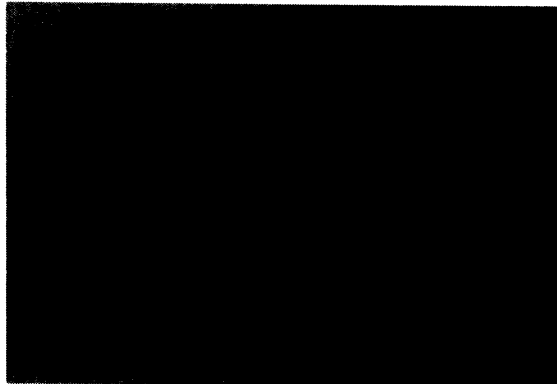
Comparison of hysteresis loops for soft and hard magnetic materials.

	Soft magnetic material	Hard magnetic material
Saturation magnetisation	As high as possible (0.8-2T)	As high as possible (0.2-1.5T)
Coercive force	As low as possible (< 100 A/m)	As high as possible (80-400 kA/m)
Permeability	As high as possible 10000-200000	Not important
Losses	As low as possible, frequency dependence	Area of loop \approx stored energy as high as possible
Shape of loop	Important because determines application	Important should be rectangular
Remanence	Not important	As high as possible
Conductivity	Determines ac-losses	Important for magnetising procedures

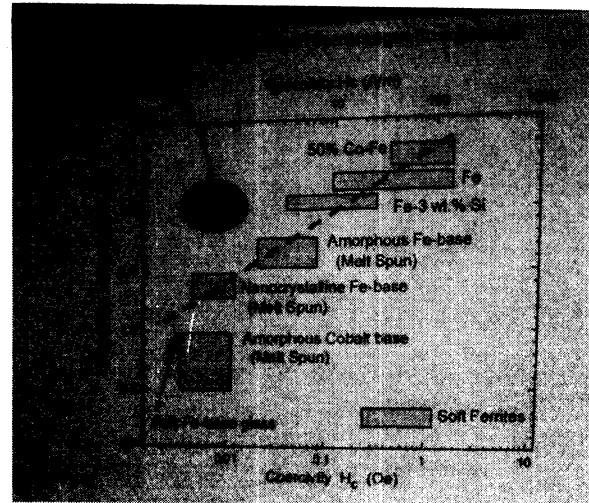
DEVELOPMENT OF NEW MAGNETIC MATERIALS FOR APPLICATIONS:

- a) intrinsic magnetic properties:
 - saturation magnetization
 - Curie temperature
 - magnetocrystalline anisotropy
 - saturation magnetostriction
 - for large M_s and T_C use of Fe or Co (or Fe-Co) alloys.
 - anisotropy and magnetostriction: sensitively dependent on alloy chemistry
- b) extrinsic magnetic properties:
 - grain size, shape and orientation, defect concentrations, compositional inhomogeneities

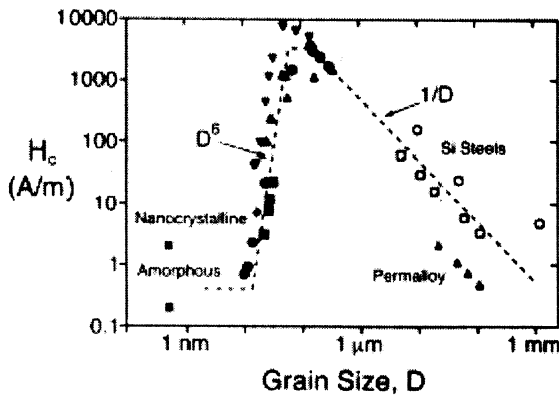
The figures below show the coercivity as function of the grain size for hard (left) and soft (right) magnetic materials:



G. C Hadjipanayis, J. Magn Magn. Mater. 200 (1999) 373



R. Schwarz, ANMM 2003, Iasi, Rumania



Herzer, G., in Handbook of Magnetic Materials, ed. Buschow, K.H.J., Vol. 10 Chap. 3, p. 415.

Amorphous alloys \neq not any long-range atomic order \neq atomic positions do not have crystalline periodic order (frozen liquid). high resistivity, low magnetocrystalline anisotropy.

Nanocrystalline alloys: term 'nanocrystalline alloy' \neq grain diameters range from 1 ± 50 nm
 Composition: $TM_{1-x}(M, NM, T)_x$; where x is around 0,2
 TM = Co, Ni, or Fe; M = B, P, Si, etc
 NM = Cu, Ag, Au, etc; T = Zr, Nb, Hf, Ta, etc.

Nanocrystalline materials: nanocrystals + residual amorphous phase
 relatively high resistivity (50 ± 80 mW cm),
 low magnetocrystalline anisotropy
 increased mechanical strength.

AC MAGNETIC RESPONSE

Magnetic loss mechanisms in soft magnetic materials:

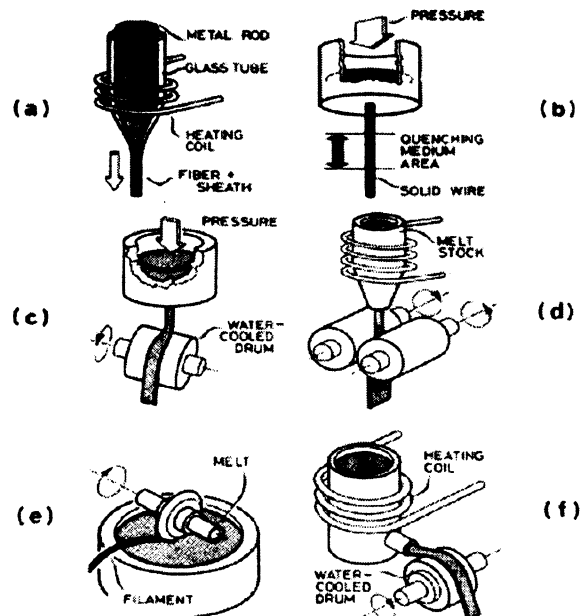
- hysteresis loss \neq due mainly to irreversible domain wall motion
- eddy current loss \neq dF/dt inducing voltages in the core material

with consequent V^2/R power loss appearing as heat.

$$R_{\text{amorphous materials}} > R_{\text{nanocrystalline materials}} > R_{\text{crystalline materials}}$$

Structure sensitive magnetic properties: depend on defect concentration, atomic order, impurities, second phases, thermal history, etc.

PRODUCTION OF AMORPHOUS MATERIALS



- Melt spinning, rapidly solidification
- sputtering
- splat cooling
- vapour deposition
- atomisation
- mechanical alloying or milling

PRODUCTION OF BULK AMORPHOUS MATERIALS

- conventional solidification with slower cooling rate due to large glass forming ability
Ex.: Fe-Al-Ga-P-C-B \bar{p} 200 mm thickness, 2 mm diameter

CAUSES OF THE HIGH THERMAL STABILITY OF THE BULK AMORPHOUS ALLOYS:

- More efficient dense random packing of constituents with different atomic sizes among P, C, and B.
- Higher energy barriers for the precipitation of Fe-M compounds due to strong interactions between P, C, and/or B and Al.
- Higher barriers to formation of Fe-B and Fe-C compounds due to Ga additions which are soluble in Fe but non miscible with B or C.

PRODUCTION OF NANOCRYSTALLINE MATERIALS

Generally, initially one obtains material in the amorphous state and subsequently crystallised by annealing.

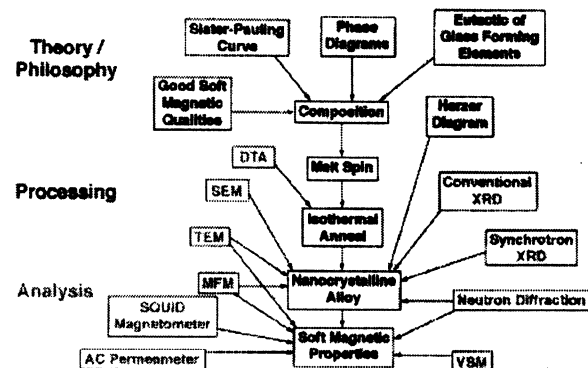


Diagram for developing a nanocrystalline soft and hard magnetic materials from an amorphous precursor (adapted from M.E. McHenry et al., *Progress in Materials Science* 44 (1999) 291-433)

NANOCRYSTALLINE MATERIALS

- **Soft materials:** contain two or more phases
- **Permanent magnets:** Two types:
 - a) single nanocrystalline hard magnetic phase
 - b) nanocomposites: known as spring magnets (hard + soft magnetic phases)

Spring magnets (hard + soft magnetic phases): $M_S(\text{soft}) > M_S(\text{hard})$.

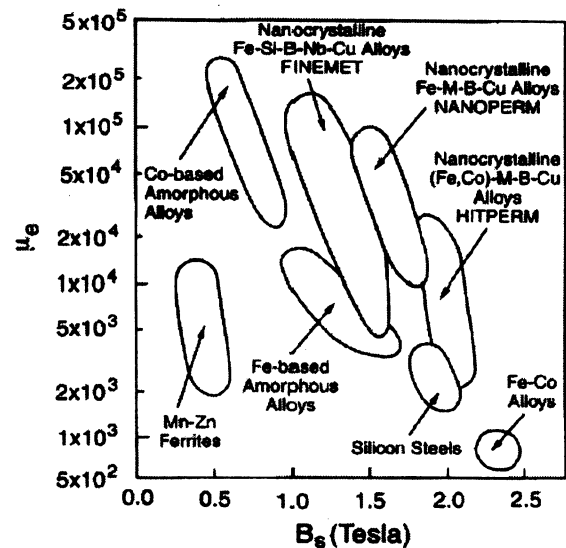
Enhancement of remanence due to: exchange coupling + high $M_S(\text{soft})$

Remanence increases however coercivity decreases.

\Rightarrow both exchange coupling between magnetic nanograins through soft magnetic matrix (amorphous or grains).

Examples of Soft Nanocrystalline Materials

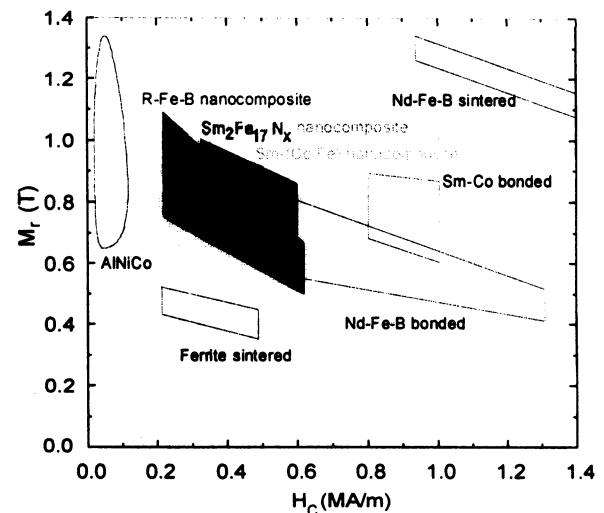
Name	Composition	Nanoparticles	$M_S(T)$	$T_c(^{\circ}C)$
FINEMET	$Fe_{73.5}Si_{13.5}Nb_3Cu_1B_9$	α -FeSi; FeSi(DO_3)	1.0-1.2	<770
NANOPERM	$Fe_{88}Zr_7Cu_1B_4$	α -Fe(BCC)	1.5-1.8	770
HITPERM	$Fe_{44}Co_{44}Zr_7Cu_1B_4$	α -FeCo(BCC) α' -FeCo(B2)	1.5-2.1	>965



Relationship between permeability, μ_e (at 1 kHz) and saturation polarisation for soft magnetic materials (A. Makino et al. *Mat Trans JIM* 1995;36:924)

HARD MAGNETIC MATERIALS

The nanocrystalline magnets do not exceed the magnetic properties of the best rare earth magnets.



MODELING

Soft Magnetic Nanocrystalline Materials

An explanation of the soft magnetic behavior and also of the dependence of the coercivity on the grain size was given by Herzer using a random anisotropy model. Figure below shows the schematic representation of this model. The model shows that the magnetic exchange length has to be larger than the grain size.

The magnetic properties are influenced by the averaging effect of the ferromagnetic exchange interaction on the local magneto-crystalline anisotropy energy. For large grains the local magnetization follows the local easy magnetic directions and the magnetization process is determined by the mean value of the magneto-crystalline anisotropy.

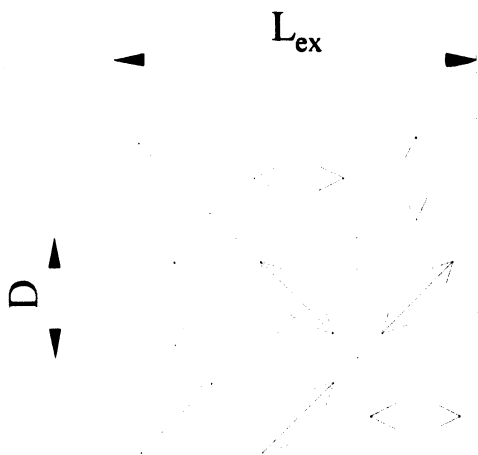
For very small grains the magnetic exchange interaction forces the magnetic moments to align parallel. Therefore the magnetization can not follow the easy directions of each individual grain. So the effective anisotropy is an average over several grains and therefore drastically reduced in magnitude.

$$N = (L_{ex}/D)^3$$

$$\langle K \rangle = \frac{K_1}{\sqrt{N}}$$

The critical parameter differentiating these two cases is given by the ferromagnetic exchange length:

$$L_{ex}^0 = (A/K_1)^{1/2}$$



Schematic presentation of the random anisotropy model with grain size D and the magnetic exchange length L_{ex} . The arrows indicate the local easy axis of magnetization.

In this equation A denotes the exchange stiffness and K_1 is the magneto-crystalline anisotropy. The averaged anisotropy can be described by the random anisotropy model. For a three-dimensional structures the grain size dependence of the average anisotropy is given by D^6 . The coercivity as well as the initial permeability must be closely correlated to the average anisotropy $\langle K \rangle$:

$$H_c = p_c \frac{\langle K \rangle}{J_s} \approx p_c \frac{K_1^4 D^6}{J_s A^3}$$

$$\mu_i = p_\mu \frac{J_s^2}{\mu_0 \langle K \rangle} \approx p_\mu \frac{J_s^2 A^3}{\mu_0 K_1^4 D^6}$$

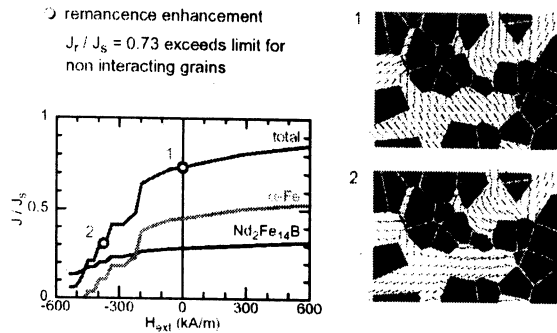
The parameters p_c and p_μ are factors close to unity. It was found [38] that the experimental dates for coercivity and permeability are compatible with the expected D^6 dependence for grain sizes below $40 \text{ nm} \approx L_{ex}$. Therefore the soft magnetic properties can be improved by reducing the grain size (only valid for $D < D_{crit}$). The dependence of the coercivity on the grain size is shown in Figure 6. [40]. It must be noticed that only an average grain size D can be determined, but a real material has a grain size distribution.

Nanocomposites

The nanocrystalline magnets with an enhanced remanence can be divided into: single nanocrystalline hard magnetic phase and nanocomposites known also as spring magnets.

Generally, the phases for the nanocomposites are composed of a hard magnetic phase and a soft magnetic phase. The soft magnetic phase should have a higher saturation magnetization than the hard magnetic phase in order to enhance the remanence even more than the nanocrystalline single phase material. The further enhancement of the remanence is due to the fact that the hard magnetic phase is polarizing the soft magnetic phase. Higher remanence is gained in cost of a decrease of the coercivity. The nanocomposite magnets show an increase of the $(BH)_{max}$ compared to the nanocrystalline single phase materials due to the higher enhancement of the remanence. However, nanocomposite magnets are limited by the low coercivity, normally less or equal to the required H_c of $0.5J_r/m_0$.

Applying a finite element modeling allows the calculation of the optimum conditions for the formation of a nanocomposite. As an example we show the results of such a model calculation in the figures below. The right side shows the domain structure at the two different working points (1) and (2). One can also see that the total demagnetizing curve is not just the superposition of that of the Nd-Fe-B and the a-Fe phase.



Finite element modeling assuming a mean grain size of 10 nm with 50 % $\text{Nd}_2\text{Fe}_{14}\text{B}$ and 50% $\alpha\text{-Fe}$ (Fidler J., Schrefl T., *Journal of Physics D: Applied Physics* 2000, 33, R135-R156)

Applications of Soft Magnetic Materials

- a) Power devices (low losses):
 1. power transformers;
 2. magnetic shields;
 3. acoustic delay lines;
 4. tensile stress transducers;
 5. transverse filters.

- b) Electronics (saturation inductions, permeabilities, hysteretic and eddy current losses and magnetoelastic properties):
 1. 400 Hz power transformers;
 2. Inductive components for switched mode power supplies;
 3. Magnetic shields;
 4. Magneto-elastic transducers;
 5. Magnetic heads for data storage applications;
 6. Magnetic springs;
 7. Acoustic-magnetic systems.

Applications of Nanocomposites

1. as magnetic component of resin-bonded magnets
2. in motor: e.g. internal permanent magnet type of rotor; multi-pole rotor used in a stepping motor.

Advantages of Nanocomposite Over Conventional Isotropic Magnets

1. Stability of the powders both in physical and chemical aspects
2. Availability of relatively fine particles sizes for molding small parts and for injection molding process,
3. Negligible long-term structural losses,
4. Relatively spherical (or non-flake-like) particle shapes,
5. Tailoring of magnetic properties