AMORPHOUS AND NANOCRYSTALLINE MATERIALS FOR APPLICATIONS AS HARD AND SOFT MAGNETS

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Outline

1) Comparison soft- and hard magnetic materials
2) Basic properties of magnetic materials
3) Production methods of amorphous and nanocrystalline materials
4) Modeling
5) Applications
**Soft magnetic materials**

**Hard magnetic materials**

Magnetic characterization: hysteresis loop

- **Range of irreversible magnetization**
- **Range of rotation magnetization**
- **Range of approach to saturation**
- **Initial permeability range**

**Coercivity**: reverse field needed to drive the magnetization to zero after being saturation

Remaining magnetization when the driving field is dropped to zero
**Soft magnetic material**  
*Coercive force* low

**Hard magnetic material**  
*Coercive force* High (higher than 80 kA/m)
<table>
<thead>
<tr>
<th>Property</th>
<th>Soft magnetic material</th>
<th>Hard magnetic material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturation magnetisation</td>
<td>As high as possible (0.8 – 2T)</td>
<td>As high as possible (0.2 – 1.5T)</td>
</tr>
<tr>
<td>Coercive force</td>
<td>As low as possible (&lt; 100 A/m)</td>
<td>As high as possible (80 – 400 kA/m)</td>
</tr>
<tr>
<td>Permeability</td>
<td>As high as possible 10000 – 200000</td>
<td>Not important</td>
</tr>
<tr>
<td>Losses</td>
<td>As low as possible, frequency dependence</td>
<td>Area of loop $\cong$ stored energy as high as possible</td>
</tr>
<tr>
<td>Shape of loop</td>
<td>Important because determines application</td>
<td>Important and should be rectangular</td>
</tr>
<tr>
<td>Remanence</td>
<td>Not important</td>
<td>as high as possible</td>
</tr>
<tr>
<td>Conductivity</td>
<td>Determines ac-losses</td>
<td>Important for magnetising procedure</td>
</tr>
</tbody>
</table>
Development of NEW magnetic materials for applications:

♥ intrinsic magnetic properties:

- saturation magnetization
- Curie temperature
- magnetocrystalline anisotropy

for large $M_s$ and $T_C$ ⇒ use of Fe or Co (or Fe-Co) alloys (Slater Pauling curve).

♥ extrinsic magnetic properties:

- grain size, shape and orientation,
- defect concentrations, compositional inhomogeneities,
Relation between coercivity and grain size

Hard

Soft


Amorphous alloys ⇒ not any long-range atomic order ⇒ atomic positions do not have crystalline periodic order (frozen liquid).

Nanocrystalline alloys:

term ‘nanocrystalline alloy’ ⇒ grain diameters range from 1±50 nm
Properties of various soft ferromagnetic materials

Schwarz, ANMM 2003, IASI, Rumenia
Comparison of the magnetic properties for different hard magnetic materials
Hard magnetic materials: Nd-Fe-B - energy product above 450 kJ/m³ achieved!

Soft magnetic materials: Fe-Si (about 3% Si) still most important.

Further improvement - new compounds!

Hard magnetic materials: nanocrystalline, nanocomposite materials
Soft magnetic materials: Amorphous materials: ribbon, wire and bulk materials
Nanocrystalline materials
Soft magnetic amorphous materials:

Composition: $\text{TM}_{1-x}(\text{M, NM, T})_x$; where $x$ is around 0.2

$\text{TM} =$ Co, Ni, or Fe; $\text{M} =$ B, P, Si, etc
$\text{NM} =$ Cu, Ag, Au, etc; $\text{T} =$ Zr, Nb, Hf, Ta, etc.

It exists hard magnetic amorphous materials?

Bulk: $\text{Nd}_{60}\text{Fe}_{30}\text{Al}_{10}$; $\text{Nd}_{60}\text{Fe}_{20}\text{Co}_{10}\text{Al}_{10}$ amorphous?
Sof magnetic nanocrystalline materials

nanocrystals + a residual amorphous phase

Magnetisation

Applied field

exchange coupling between magnetic nanograins through amorphous matrix)
Examples of soft nanocrystalline materials

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition</th>
<th>Nanoparticles</th>
<th>$M_s$ (T)</th>
<th>$T_C$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FINEMET</td>
<td>$Fe_{73.5}Si_{13.5}Nb_{3}Cu_{1}B_{9}$</td>
<td>$\alpha$-FeSi;FeSi(DO$_3$)</td>
<td>1.0-1.2</td>
<td>&lt;770</td>
</tr>
<tr>
<td>NANOPERM</td>
<td>$Fe_{88}Zr_{7}Cu_{1}B_{4}$</td>
<td>$\alpha$-Fe(BCC)</td>
<td>1.5-1.8</td>
<td>770</td>
</tr>
<tr>
<td>HITPERM</td>
<td>$Fe_{44}Co_{44}Zr_{7}Cu_{1}B_{4}$</td>
<td>$\alpha$-FeCo(BCC); $\alpha'$-FeCo(B2)</td>
<td>1.5-2.1</td>
<td>&gt;965</td>
</tr>
</tbody>
</table>
Relationship between permeability, $\mu_e$ (at 1 kHz) and saturation polarisation for soft magnetic materials

(A. Makino et al. Mat-Trans JIM 1995;36:924)
AC magnetic response

- eddy current loss $\Rightarrow$ loss appearing as heat in the core material with consequent $V^2/R$.

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

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

Non Magnetic properties: mechanical, corrosion, resistivity

Time dependence of the initial susceptibility (disaccommodation) and the stress dependence of the permeability ⇒ sensitive to quench rate (PECO-Project; R. Sato Turtelli et al. Phys. Rev. B, 63 (2001) 094427-1-8).

Production of amorphous, bulk amorphous and nanocrystalline materials
**Melt Spinner**: To form the amorphous phase, the material must be cooled from melting temperature $T_m$, to the glass transition $T_g$, without any crystallization.

*Schematic and machine of a melt-spinning apparatus used to produce amorphous metallic ribbons (Siemens)*
Other methods of the 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 ⇒ 200 μm 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 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.
Experimental observations in bulk amorphous alloys

Fe-Al-Ga-P-C-B-Si

Relative resistance measured in situ on the ribbon as a function of time during JH experiment as obtained with different current densities.

Coercive field as function of the current density of Fe\textsubscript{73}Al\textsubscript{5}Ga\textsubscript{2}P\textsubscript{11-x}C\textsubscript{5}B\textsubscript{4}Si\textsubscript{x} (x = 0, 1, 3) samples obtained at room temperature.
Production methods of magnetic 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)
Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$
VAC E 4229/2
f = 5 kHz
$H_{ac} = 0.05$ A/m

annealing 1 h
Temperature dependence of the coercivity of FINEMET obtained from annealing the amorphous ribbons produced with different quenching rates.
Grain size dependence


Herzer considers:

a) grain size $D <$ exchange length $L_{ex}$

b) effective anisotropy is average over several grains – reduced anisotropy

c) characteristic volume whose linear dimension is the magnetic exchange length, $L_{ex} \sim (A/K)^{1/2}$. (Volume $\propto L_{ex}^3$).

d) $N$ grains, with random easy axes, within a volume of $L_{ex}^3$ to be exchange coupled.

In these conditions:
The effective anisotropy is: \( K_{\text{eff}} = K/N^{1/2} \) and the number of grains in this exchange coupled volume is: \( N = (L_{\text{ex}}/D)^3 \). Then:

\[
K_{\text{eff}} = KD^{3/2} \sim \left( \frac{K_{\text{eff}}}{A} \right) \sim \left( \frac{K^4 D^6}{A^3} \right)
\]

Since \( H_c \) can be taken as proportional to \( K_{\text{eff}} \):

\[
H_c \sim H_K \sim D^6
\]

\[
H_c = p_C \frac{K_1^4 D^6}{J_s A^3}
\]

\[
\mu_i = p_\mu \frac{J_s^2 A^3}{\mu_0 K_1^4 D^6}
\]

For sufficiently small nanocrystals \( \Rightarrow \) superparamagnetic
Permanent magnets: ⇒ Two types:
♦ single nanocrystalline hard magnetic phase
♦ nanocomposites: known as spring magnets (hard + soft magnetic phases).

⇒ exchange coupling between magnetic nano-grains through soft magnetic grains.
Spring magnets (hard + soft magnetic phases): $M_s$(soft) > $M_s$(hard).

Enhancement of remanence due to: exchange coupling + high $M_s$(soft)

Remanence increases however coercivity decreases.

After Davies *at al*
Exchange coupling leads to a remanence enhancement!

Theoretical limit for the maximum energy product, \((BH)_{\text{max}}\) is:

\[
(BH)_{\text{max}} \leq \frac{J_s^2}{4 \mu_0}
\]

Remanence for a polycrystalline magnet - non-interacting isotropic, uniaxial grains:

\[
J_r = J_s \frac{\int_{0}^{2\pi} \int_{0}^{\pi} \cos \theta \sin \theta d\theta d\phi}{\int_{0}^{2\pi} \int_{0}^{\pi} \sin \theta d\theta d\phi} = \frac{1}{2} J_s
\]

Nanocrystalline material due to exchange coupling - for isotropic material \(J_r/J_s > 0.5\) is possible!
Nanocrystalline materials

For nanocrystalline material the way how the small grains are coupled is of great importance for the understanding of the remanence enhancement. For grains of nano-size different exchange length have to be considered:

Exchange length due to external field: \( \ell_H = \sqrt{\frac{2A}{H \cdot \mu_0 \cdot M_s}} \)

Exchange length due to crystal energy: \( \ell_K = \sqrt{\frac{A}{K}} \)

Exchange length due to stray fields: \( \ell_s = \sqrt{\frac{2\mu_0 A}{\left(\mu_0 \cdot M_s\right)^2}} \)

Which type of “exchange length” is more important, it depends on the material.
Hard magnetic materials

Modeling: Finite element modeling for nanocomposite to obtain a remanence enhancement

- Two-phase magnet with residual amorphous phase
  - Mean grain size = 10 nm
  - Width of intergranular phase = 3.2 nm
  - Reduction of exchange constant = 0.2

\[ \frac{J_r}{J_s} = 0.73 \] exceeds limit for non-interacting grains
Advantages of nanocomposite over conventional isotropic magnets

# Stability of the powders both in physical and chemical aspects

# Availability of relatively fine particles sizes for molding small parts and for injection molding process,

# Negligible long-term structural losses,

# Tailoring of magnetic properties
Applications of soft magnetic materials

**Power devices (low losses):**
- power transformers
- magnetic shields
- acoustic delay lines
- tensile stress transducers
- transverse filters.

**Electronics** ($M_s$, $\mu$, eddy current and magnetoelastic properties):  
- 400 Hz power transformers;  
- Inductive components for switched mode power supplies;  
- Magnetic shields;  
- Magneto-elastic transducers;  
- Magnetic heads for data storage applications;  
- Magnetic springs;  
- Acoustic-magnetic systems.
(a) 60 Hz distribution
(b) Ribbon wound cruciform distribution transformer applications (Suzuki et al, Mat. Sci. Eng. 1994)
Acoustic-magnetic systems
Applications of nanocomposites

- as magnetic component of resin-bonded magnets

- in motor: e.g. internal permanent magnet type of rotor; multi-pole rotor used in a stepping motor.

- Medical applications

- in oil pollution in the sea
Prof. P. C. Morais (Univ. Brasilia) 2003