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28. Nanostructured Magnetic Materials

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Contents:

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1. Summary

Nanostructured metallic and ceramic materials have unique mechanical and magnetic properties. Currently numerous programs attempt to tailor advanced structural and functional nanostructured materials. Among various studies, nanostructured magnetic materials have been successfully fabricated during the past decade using an amorphous precursor processing method. Major magnetic alloy systems satisfy three empirical requirements to produce the amorphous precursor:

- The alloys are composed of more than ternary systems.
- Constituent alloying elements possess significantly different atom size.
- The heat formation of amorphous alloys is negative.

During the amorphous precursor processing of advanced magnetic alloys, partial and full transformations of amorphous precursors prepared by melt spinning into nanocrystalline phases can be achieved without introducing impurities and defects. Recent advancements in transmission electron microscopy (TEM), high-resolution electron microscopy (HREM) and three-dimensional atom probe (3DAP) techniques assist understanding the role of nanostructure in improving the magnetic properties. Hono and Ohnuma recently highlighted the significance of studying the composition/structure/property relationship of nano-structured magnetic materials (*Magnetic Nanostructures,* edited by H. S. Nalwa, Amer. Sci. Pub., 2002, p. 1). Their review paper is summarized as follows.

Soft Magnetic Nanocrystalline Materials

Grain Size Effect

The coercivity (H_c) in soft ferromagnetic materials strongly depends on the grain size (d), as shown in Fig. 1. The critical grain size (d_c) of about 40 nm, which is nearly the same as the domain wall thickness, divides two regimes. When $d > d_c$, H_c inversely increases as the grain size is decreased. This is related to an increase in the magneto-crystalline anisotropy. Below d_c, H_c very rapidly decreases with decreasing grain size, obeying the law of $H_c \approx d^6$ proposed by Hertzer (*IEEE Trans. Mag.*, **26**, 1397, 1990), and reaches down to the level of 1 A/m. The grain refinement ($d < d_c$) diminishes the magneto-crystalline anisotropy due to the averaging effect of magnetization over randomly oriented nanosized grains, leading to a reduction of H_c. Such magnetic behavior is similar to the dependence of mechanical strength on the grain size. They can be understood in terms of analogous effects of the grain size on the motion of domain walls and dislocations, respectively, under magnetic and stress fields. The characteristics of various soft magnetic nanostructured materials are illustrated in Fig. 2. There is a decreasing trend of the permeability (μ_i) with increasing saturation magnetic flux (B_s) and H_c in different classes of advanced soft magnetic materials. The shaded area indicates the nanostructured magnetic materials summarized in this report.

Fe-Si-B-Nb-Cu System (FINEMET)

Yoshizawa et al. (*J Appl. Phys.*, **64**, 6044, 1988) invented a 73.5at.%Fe-13.5at.%Si-9 at.%B-3at.%Nb-1at.%Cu alloy (FINEMET) with better soft magnetic properties, i.e., H_c = 0.5-1 A/m and $\mu_i = 0.7\text{-}1 \times 10^5$ except lower B_s (=1.2 T), than amorphous Fe-Si-B alloys and oriented Si-steels. Annealing at 500-600°C for 1 h partially transforms as-quenched amorphous phases into nanostructure. Detailed TEM and 3DAP analysis have shown that the nanostructure is composed of three components: (i) Nanocrystalline α-Fe phase (d = 10-15 nm) contains 20at.%Si and a few at.% B; (ii) Fe-based amorphous phase, which occupies 20-30% of the volume fraction, is enriched in B and Nb with a small Si; (iii) Cu particles are dispersed. Embedding the nanocrystalline phase into the amorphous phase causes lowering H_c and enhancing μ_i. The magneto-elastic anisotropy in the FINEMET alloy is suppressed by balancing the negative and positive magnetostriction of the nanocrystalline and amorphous phases. We can see the difference in the magnetostriction coefficient (λ_s) between the amorphous and nanostructured state in Fig. 3. The nanostructure is built-up due to the combined effects of Cu and Nb, which slightly dissolve in the bcc phase. During the precursor annealing, Cu clustering heterogeneously occurs, which serves as nuclei of α-phases, while the presence of Nb hinders the precipitation of hard magnetic Fe_2B. Both Cu and Nb impede the grain growth. In a modified Fe rich alloy (77at.%Fe-11at.%Si-9at.%B-2.4at.%Nb-0.6 at.%Cu) with higher B_s (=1.4 T) and μ_i (=1.5 x10^5), the optimal Cu content becomes smaller than that in the premier FINEMET alloy. The reason for this is that the Fe rich alloy has a lower crystallization temperature and weaker dependence of Cu clustering temperature on the heating rate.

Fe-Zr-B System (NANOPERM)

Soft magnetic (86-91)at.%Fe-7at.%Zr-(7-2)at.%B alloy systems with B_s =1.5 T and similar H_c and μ_i to the FINEMET are developed as NANOPERM, which are composed of nanocrystalline α-Fe phases with a small volume fraction of amorphous phases enriched in B and Zr. The drawback of Fe-Zr-B system alloys is that the amorphous precursor processing must be carried out in vacuum due to the poor oxidation resistance. Although the Cu addition is not required for the nanocomposite unlike the FINEMET, it causes uniform dispersion of nano-phases due to the Cu clustering. The addition of Si improves the permeability by minimizing the magneto-elastic anisotropy of the nanostructured Fe-Zr-B alloy. As shown in Fig. 3, however, the dependence of λ_s on the Si content is quite different in the FINEMET and NANOPERM alloys. While Si dissolved only in the α-Fe phase directly reduces the magnetostriction in the Fe-Si-B-Nb-Cu system, Si partition occurs between the α-Fe and Zr rich amorphous phase in the Fe-Zr-B-Si alloy. Such difference is ascribed to a stronger attractive interaction of Si with Zr than with Fe. In the NANOPERM system, hence, λ_s slightly increases from the negative with increasing Si and it becomes positive when the Si content exceeds 4 at%. Partial replacement of Fe by Co is effective in increasing B_s and Curie temperature. A 44at.%Fe-44at.%Co-7at.%Zr-4at.%B-1at.%Cu alloy (HITPERM), consisting of nanoscale α-FeCo particles and residual amorphous phases, maintains the ferromagnetic behavior up to 900^{o}C.

Hard Magnetic Nanocrystalline Materials

Two research groups made a breakthrough in developing a new Nd containing permanent magnetic material two decades ago. Sagawa et al. (*J Appl. Phys.*, **55**, 2083, 1984) fabricated a 15at.%Nd-77at.%Fe-8at.%B alloy with d = 15μm, composed of major $Nd_2Fe_{14}B$ (11.7at.%Nd-82.3at.%Fe-5.9at.%B) phase and minor Nd rich (> 80at.%) phase along the grain boundaries, using a powder sintering method. The Nd rich hard magnetic alloy possesses much higher H_c (= 960 kA/m), remanence (B_r = 1.2 T) and hysteresis loss [$(BH)_{max}$ = 290 kJ/m^3] than nano-grained (50 nm) 13.5at.%Nd-81.7at.%Fe-4.7at.%B alloys prepared by the melt-spinning method (J. Croat et al., *J Appl. Phys.*, **55**, 2078, 1984). Since then, extensive efforts are being made to produce economical nanostructured Nd lean permanent magnet alloys.

$Fe_3B/Nd_2Fe_{14}B$ systems

Coehoon et al. (J. Physics, Paris, **49**, 669, 1988) have produced a hard nanocomposite magnet (4.5at.%Nd-77.5at.%Fe-18.5at.%B), made up of soft Fe_3B and hard $Nd_2Fe_{14}B$ magnetic phases. The mixture of soft and hard nanostructured phases brings about a sufficiently high B_r due to the large exchange interaction. When the grain size is too small, however, the magnetic anisotropy of hard magnetic phases becomes weak, leading to a reduction in H_c. Thus, there is an optimum grain size to compromise H_c and $(BH)_{max}$. A 3.25at.%Nd-1at.%Tb-71.15at.%Fe-5at.%Co-0.5at.%Cu-0.5at.%Nb-18at.%B alloy with H_c =

424 kA/m and $(BH)_{max}$ = 100 kJ/m^3 with equal amounts of soft and hard phases recently has been recently developed by Bernandi and co-workers (*J. Magn. Magn. Mater*., **219**, 186, 2000). The partial replacement of Nd by Tb and that of Fe by Co increase the intrinsic coercivity but have no effect on the nanostructure. The addition of Cu and Nb improves the permanent magnetic properties by refining the $Fe_3B/Nd_2Fe_{14}B$ phases. Ping et al. (Acta Mater., **47**, 4641, 1999) have clarified the mechanism by applying the HREM and 3DAP method. In a similar manner to the soft magnetic alloys, the formation of Cu clusters facilitates the primary precipitation of Fe_3B phases. Moreover, B segregation and Nb depletion at the interface of Nd enriched Cu cluster/amorphous phase assists the formation of Fe_3B.

α-Fe/$Nd_2Fe_{14}Bn$ systems

Another type of permanent magnets is composed of α-Fe/$Nd_2Fe_{14}B$. In such alloys, melt-spinning process does not fully produce amorphous phases so that controlling the nanostructure and magnetic properties would become difficult. In fact, H_c of the α-Fe/$Nd_2Fe_{14}B$ alloy highly varies depending on the cooling rate of melt spinning affecting the crystallization process. An 8at.%Nd-76at.%Fe-8at.%Co-2at.%Nb-6at.%B alloy, composed of α-Fe/$Nd_2Fe_{14}B$ and some amorphous phases, has better hard magnetic properties than the $Fe_3B/Nd_2Fe_{14}B$ systems (Hamano et a., Proc. 5^{th} Inter. Workshop on Rare Earth Magnets and their Application, Informationsgesellschft, Dresden, 1998, p.199). The enrichment of Nb stabilizes amorphous phases near the α-Fe/$Nd_2Fe_{14}B$ interface. The amorphous phase adjacent to the interface causes the grain refinement, thereby strengthening the exchange interaction of soft and hard grains and increasing H_c. Unlike the soft FINEMET and NANOPERM, and hard $Fe_3B/Nd_2Fe_{14}B$, however, the Cu addition is not effective in refining the grain of α-Fe/$Nd_2Fe_{14}B$.

2. Background

The magnetic coercivity and mechanical strength have analogous dependence on the grain size. This suggests that the motion of domain walls and dislocations interact similarly with grain boundaries under magnetic and stress fields. While the nanostructured magnetic materials have several advantages over conventional alloys, a poor ductility problem exists for high strength nano-grained materials when used for mechanical parts.

3. Assessment

Amorphous precursor processing is a viable route to develop soft and hard magnetic nanostructured materials. The technique has a greater advantage over other processing, such as consolidation of mechanically alloyed powers and heavy deformation that yield impurity precipitation and structural defects. A number of Japanese scientists, who excel in the field of magnetic materials since Prof. Honda invented the KS permanent magnet in 1916, have made great contributions to the advancement of nanostructured magnetic materials. While extensive experimental studies enhance fundamental understanding of magnetization in nanostructured materials, the theoretical analysis is still far behind due to the complex magnetic alloy systems, which make it difficult to model the magnetic behavior.

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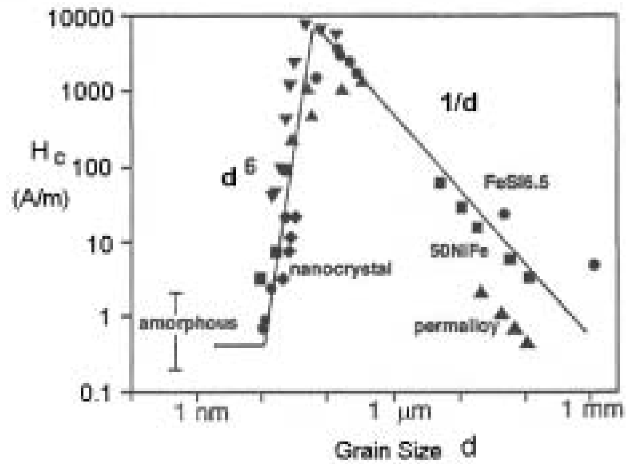

Fig.1. Grain size dependence of coercivity (H_c) in various soft ferromagnetic materials

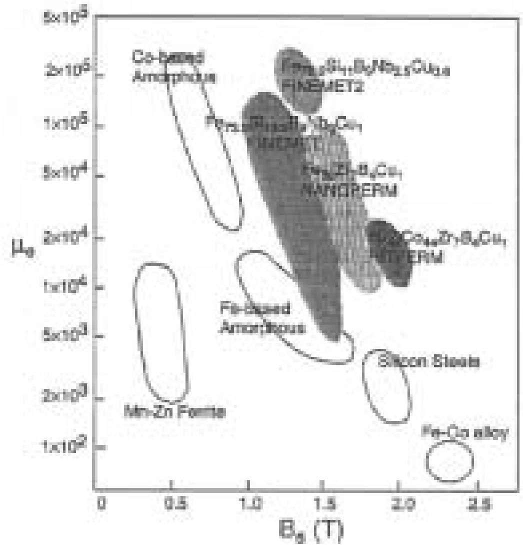

Fig. 2. Characteristics of various nanostructured soft magnetic materials.

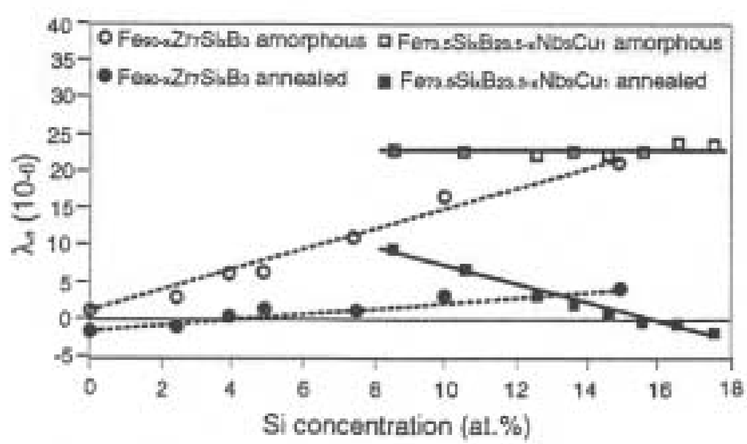

Fig. 3. Variation of magnetostriction coefficient (λ_s) to Si content in 73.5at.%Fe-(x)at.%Si-(23.5-x)at.%B-3at.%Nb-1at.%Cu (FINEMET) and (90-x)at.%Fe-7at.%Zr-(x)at.%Si-3at.%B (NANOPERM) alloys: Open and closed points indicate the as-quenched and annealed (500^{o}C) state.