Modern soft magnets: Amorphous and nanocrystalline materials

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Abstract

This article surveys amorphous and nanocrystalline alloys for soft magnetic applications. Both materials have much in common, starting from the technique of production and including the key factors that determine their properties. Thus the magneto-crystalline anisotropy randomly fluctuates on a scale much smaller than the domain wall width and, as a consequence, is averaged out by exchange interactions so that there is no net anisotropy effect on the magnetization process, the prerequisite for good soft magnetic behaviour. Superior soft magnetic properties additionally require low magnetostriction, which is true of amorphous Co-based alloys and, more recently, nanocrystalline Fe-based alloys, but at a significantly higher saturation induction and with better thermal stability. Both materials reveal low losses of up to several hundred kilohertz and their B–H loop can be tailored by magnetic field annealing according to the demands of the application.

Keywords: Amorphous; Anisotropy; Magnetization process; Magnetostriction; Nanocrystalline

1. Introduction and background

Soft magnetic materials are, by definition, characterized by low coercivity. Typical examples are shown in Fig. 1 [1]. Among soft magnetic materials unalloyed iron and Fe–Si alloys are employed in the largest quantities, with a market share of about 80%. They are mainly used for the generation and distribution of electrical energy, with applications in motors taking a prominent part. However, eddy current losses can become a limiting factor at elevated frequencies. Thus high frequency applications are the classical domain of soft ferrites based on MnZn (1–1000 kHz) or NiZn (1–1000 MHz). Apart from these mass products there is a relatively small but important niche of soft magnetic speciality alloys. Examples are crystalline CoFe alloys with particularly high saturation magnetization and crystalline NiFe alloys characterized by high permeability and low coercivity. We will focus here on the newest of these alloys, amorphous and nanocrystalline soft magnetic materials.

Amorphous metals for soft magnetic applications are produced by rapid solidification from the melt [8,9] as thin ribbons about 20 μm thick. Typical compositions are with polycrystalline NiFe alloys but they simultaneously exhibit significantly lower eddy current losses than their crystalline counterparts. This is illustrated in Fig. 2, which compares the core losses of soft magnetic materials used for high frequency power transformers [2]. It is this combination of superior soft magnetic properties and low losses in particular which has fuelled the interest in amorphous and nanocrystalline materials. Thus amorphous Fe-based alloys are becoming increasingly interesting for more efficient energy distribution [3–5] (http://www.greencarcongress.com/2008/11/hitachi-develop.html), which classically was the domain of Fe–Si steels. Their favourable high frequency behaviour up to frequencies of several hundred kilohertz has made amorphous and nanocrystalline soft magnets competitive, even with MnZn ferrites [6,7]. The low eddy current losses of wound cores of amorphous or nanocrystalline ribbons are essentially due to (1) the thin ribbon gauge d ≈ 20 μm, inherent to the production technique, and (2) a relatively high electrical resistivity of typically ρ ≈ 100–130 μΩ cm, related to the microstructure [3].

Amorphous metals for soft magnetic applications are produced by rapid solidification from the melt [8,9] as thin ribbons about 20 μm thick. Typical compositions are...
(Fe,Co,Ni)$_{70-85}$(Si,B)$_{15-30}$ at.%. The metalloids Si and B are necessary for glass formation and in order to stabilize the amorphous structure [9,10]. The detailed composition can be widely varied, which allows coverage of a large spectrum of soft magnetic properties according to the demands of the application. The production process and the resulting atomic structure are schematically sketched in Fig. 3. The microstructure is characterized by the absence of atomic long-range order and reveals only a short-range order with a structural correlation length of the order of atomic distances. It is virtually a snapshot of the random atomic arrangement of the liquid melt frozen at a cooling rate of typically $10^5$–$10^6$ K s$^{-1}$. This high cooling rate is necessary to achieve the amorphous structure and limits the upper bound of the ribbon thickness to values below about 50 µm. The final ribbon dimension is achieved from the liquid melt in a single step within a millisecond. In comparison, thin sheets of conventional metallic alloys require a series of hot and cold rolling steps. This means that the production process becomes more difficult and more expensive the thinner the final gauge gets.

Nanocrystalline soft magnetic materials start as an amorphous ribbon. The nanocrystalline state is achieved by a subsequent heat treatment above the crystallization temperature. Hitherto the crystallization of amorphous metals was known to significantly degrade their soft magnetic properties and to yield a relatively coarse microstructure with grain sizes of about 0.1–1 µm. In 1988, however, Yoshizawa et al. [11] found that the crystallization of Fe–(Si,B) glasses with the addition of small amounts of Cu and Nb yields an ultrafine grain structure of bcc FeSi with grain sizes of typically 10–15 nm embedded in an amorphous matrix. Fig. 4 depicts the characteristic microstructure. These new nanocrystalline alloys have superior soft magnetic properties so far only achieved by permalloys and Co-based amorphous alloys, but at a significantly higher saturation induction of 1.2 T and more.

The combination of small grain size and soft magnetic properties was surprising and fascinating from the classical point of view in magnetic engineering. Fig. 5 summarizes the variation of the coercivity $H_c$ over the whole range of structural correlation lengths starting from atomic distances in amorphous alloys with grain sizes $D$ in the nanometer region up to macroscopic grain sizes. The permeability shows an analogous behaviour, being essentially inversely proportional to $H_c$. The $1/D$ dependence of coercivity for large grain sizes [17,19] reflects the conventional rule that...
good soft magnetic properties require very large grains ($D > 100 \mu m$). Thus the reduction in particle size to that of the domain wall width increases the coercivity $H_c$ to a maximum controlled by the anisotropies present. Accordingly, fine particle systems have been mostly discussed as hard magnetic materials [20]. The lowest coercivities, however, are again found for the smallest structural correlation lengths, as in amorphous alloys (with a "grain size" of the order of atomic distances) and in nanocrystalline alloys for grain sizes $D < 20 \text{ nm}$. Obviously, the new nanocrystalline materials fill the gap between amorphous metals and conventional polycrystalline alloys. The decrease in coercivity of nanocrystalline materials has to be distinguished from the phenomenon of superparamagnetism, i.e. the well-known decrease in coercivity of small, isolated or weakly coupled particles due to thermal excitation [20]. Although coercivity is absent, the superparamagnetic regime is not of interest for soft magnetic application since an appreciable change in magnetization requires large magnetic fields, i.e. the permeability is fairly low. In the present case we deal with small ferromagnetic crystallites coupled by exchange interactions [12,21] and with low coercivity and, simultaneously, high permeability.

Owing to their small structural correlation length, amorphous and nanocrystalline materials are not only magnetically soft but at the same time mechanically hard (a Vickers hardness of typically 800–1000 HV) and exhibit a high yield strength of around 3000 MPa [9]. This contrasts with the situation in conventional soft magnetic metals, which are known to also be mechanically soft, with yield strengths of the order of only a few hundred megapascals.

2. Basic mechanisms

The basic condition for good soft magnetic properties is a low magnetic anisotropy constant $K$, which is a measure of the energy density needed to rotate the magnetization vector out of its energetically preferred orientation (magnetic easy axis). The most important contribution is magneto-crystalline anisotropy, which is related to the symmetry of the local atomic structure. The actual microstructure leads to a distribution of magnetic easy axes varying in their orientation over the scale of the structural correlation length (grain size) $D$.

When the structural variations occur on a large scale, as in conventional polycrystalline materials, magnetization will follow the individual easy magnetic axes of the structural units. The magnetization process is thus determined by the local magneto-crystalline anisotropy constant $K_1$ of the grains. There are various concepts for minimizing the effects of magneto-crystalline anisotropy in this case: (i) an atomic structure of cubic symmetry; (ii) a microstructure with large grains; (iii) a texture with the magnetic easy axis parallel to the direction of the applied field as, for example, in oriented Si-containing steels; (iv) a composition where $K_1$ vanishes, as, for example, in 80%NiFe (permalloys).

For small structural correlation lengths, however, ferromagnetic exchange interactions start to dominate and more and more force the magnetic moments to become aligned in parallel, thus impeding magnetization following the easy axis of each individual structural unit. As a consequence the effective magnetic anisotropy will be an average over several structural units and thus will be reduced in magnitude. This is the situation in amorphous and nanocrystalline soft magnetic materials where the microstructure is characterized by a distribution of magnetic anisotropy axes randomly varying on the atomic scale in amorphous metals or on a scale of about 5–20 nm in typical nanocrystalline materials.

The degree to which the randomly oriented anisotropies are finally averaged out has been successfully addressed in terms of the so-called random anisotropy model [21], which was originally developed for amorphous metals [22].

2.1. Random anisotropy model

The random anisotropy model starts from a microstructure characterized by a distribution of magnetic anisotropy axes randomly varying their orientation over the scale $D$. The interplay between exchange and anisotropy energy is described by the free energy density

$$\phi = A \sum_{i=x,y,z} (\nabla m_i)^2 + K_1 f_K(m \cdot u)$$  \hspace{1cm} (1)

where $A$ is the exchange stiffness, $m$ is the direction of the magnetization vector, $K_1$ is the local magneto-crystalline anisotropy constant and $f_K$ is a dimensionless function describing the angular variation in the anisotropy energy density with respect to a local symmetry axis denoted by $u$.

It is evident from Eq. (1) that the exchange energy density scales as $A/L^2$ if the magnetization direction changes on length scale $L$. Consequently, the exchange energy...
would exceed the local anisotropy energy (i.e. $A/L^2 > K_1$) if the magnetization followed the local anisotropy variations on a scale smaller than

$$L_0 = \phi_0 \sqrt{A/K_1}$$

where $\phi_0$ is a dimensionless parameter of the order of one. This basic ferromagnetic correlation length represents the characteristic minimum scale below which the direction of magnetization cannot vary appreciably. It determines, for example, the magnitude of the domain wall width for which the magnitude of the domain wall width for the local anisotropy constant, which is given by the basic exchange length $L_0$ and where the local randomly oriented anisotropies are averaged by the smoothing effect of exchange interactions.

The magnetic anisotropy relevant to the magnetization process for $D < L_0$ is given by the average of the anisotropy energy density over the volume $V_{ex} = L_{ex}^3$ defined by a correlation length $L_{ex}$ within which the magnetization direction is kept constant by exchange interactions. The situation is schematically sketched in Fig. 6. The average over the randomly oriented anisotropies of the $N = (L_{ex}/D)^3$ grains in the exchange coupled volume is determined by statistical fluctuations. The average anisotropy constant $\langle K_1 \rangle$ hence scales as

$$\langle K_1 \rangle = K_1/\sqrt{N} = K_1 \cdot (D/L_{ex})^{3/2}$$

(3)

The resulting easiest magnetic axis of the $N$ grains is randomly oriented from one region of exchange coupled grains to another. The magnetization will follow these easy axes and the exchange energy consequently scales as $A/L_{ex}^2$. Accordingly, the averaged total free energy density with respect to the homogeneously magnetized state becomes

$$\langle \phi \rangle \approx A \cdot (\alpha/L_{ex})^2 - \frac{1}{2} \beta [K_1] \cdot (D/L_{ex})^{3/2}$$

(4)

Here $\alpha$ and $\beta$ are dimensionless parameters, where $\alpha$ corresponds to the average angle between the easiest axes of adjacent exchange coupled regions and $\beta$ is related to the symmetry of the random anisotropy axis [23]. Minimum $\langle \phi \rangle$ with respect to $L_{ex}$ is given for

$$L_{ex} = \phi_0 \sqrt{A/[K_1]}$$

(5)

with $\phi_0 = \alpha \sqrt{8/(3\beta)}$. The resulting exchange length $L_{ex}$ thus follows from the basic exchange length $L_0$ as defined in Eq. (2) by self-consistently substituting the average anisotropy constant $\langle K_1 \rangle$ for the local anisotropy constant $K_1$. This renormalization accounts for the fact that the scale at which exchange interactions dominate expands at the same time as the anisotropy is averaged out and, hence, the local anisotropies are averaged out even more efficiently. Combining Eqs. (3) and (5) yields

$$\langle K_1 \rangle = K_1 \cdot (D/L_0)^6$$

(6)

This final result is essentially based on statistical and scaling arguments and, therefore, is not limited to uniaxial anisotropies (as may be anticipated from Fig. 6 or from the original work of Alben et al. [22]) but also applies for cubic or other symmetries. The parameters $\alpha$, $\beta$ and $\phi_0$ remain open within this scaling analysis. Their theoretical determination would require a by far more sophisticated micromagnetic analysis of the problem. However, all these parameters can ultimately be combined in a single material constant, which is given by the basic exchange length $L_0$, i.e. the critical scale below which the averaging mechanism becomes effective.

The most significant feature predicted by the random anisotropy model is the strong variation in $\langle K_1 \rangle$ with the sixth power of the grain size. In typical nanocrystalline Fe-based alloys with grain sizes of the order of 10–15 nm, i.e. $D \approx L_0/3$, the local magneto-crystalline anisotropy $K_1 \approx 10^5$ J m$^{-3}$ is reduced by three orders of magnitude towards a few Joules per cubic metre, which is small enough to enable superior soft magnetic behaviour. Correspondingly, the renormalized exchange length $L_{ex}$ expands into the micron regime and is almost two orders of magnitude larger than the basic exchange length $L_0$ ($\sim 40$ nm). A similar estimate for amorphous transition metal-based alloys yields even lower values of the averaged anisotropy of the order of microjoules per cubic metre and less.

2.2. Multiphase systems and mixed anisotropies

The preceding arguments were based on a single phase system. In real materials, however, we deal with various structural phases. In typical soft magnetic nanocrystalline materials the randomly oriented crystallites of about 10 nm in size are embedded in an amorphous matrix. The latter is again made up of structural units with magnetic easy axes randomly fluctuating on the much smaller scale...
of atomic distances. Moreover, real materials reveal additional anisotropies, such as magneto-elastic and field-induced anisotropies, which are uniform on a scale much larger than the exchange length. Such long-range anisotropies ultimately determine the soft magnetic properties of optimized nanocrystalline alloys, in which the contribution of the random anisotropies tends to become negligible.

### 2.2.1. Mixed random and uniaxial anisotropies

The average anisotropy constant \( \langle K \rangle \) of a coupled multiphase system with anisotropies randomly oriented on a scale smaller than a magnetic correlation length \( L_{\text{ex}} \) can be described by [23]

\[
\langle K \rangle = \sqrt{K_u^2 + \sum \beta_i^2 K_{1,i}^2 \cdot (D_i/L_{\text{ex}})^3}
\]  \( \text{(7)} \)

where \( K_u \) denotes a uniaxial anisotropy, which is uniform on a scale much larger than \( L_{\text{ex}} \). The random contributions are represented by the local anisotropy constants \( K_{1,v} \), the grain sizes \( D_v \) and the volume fractions \( x_v \) of the individual structural phases labelled by the index \( v \).

The result includes a grain size distribution if the term “structural phase” is used in a more general sense for all grains with the same \( K_{1,v} \) and the same grain size \( D_v \). The parameters \( \beta \) mainly involve conventions used to define the anisotropy constants for different symmetries, but also include some statistical corrections of the order of 10–20%. Numerical simulations for single phase systems result in \( \beta \approx 1 \) for uniaxial and \( \beta \approx 0.4 \) for cubic symmetry.

The above result is valid as long as the average number of coupled grains is larger than one for each individual phase. For the derivation it is only necessary to assume that the magnetization is parallel within a specific volume defined by a correlation length \( L_{\text{ex}} \). An a priori specification of the precise coupling mechanism is not needed. This reduces the problem to adding up random anisotropies, which can be done analytically using statistical concepts, and/or by straightforward micromagnetic simulations [23,24].

If the coupling mechanism is dominated by exchange interactions the correlation length \( L_{\text{ex}} \) is self-consistently related to the average anisotropy constant \( \langle K \rangle \) by

\[
L_{\text{ex}} = \varphi \sqrt{A/\langle K \rangle}
\]  \( \text{(8)} \)

where \( \varphi \) is a pre-factor of the order of unity.

In the general case the average anisotropy \( \langle K \rangle \) has to be determined from Eqs. (7) and (8) by numerical iteration. Fig. 7 shows the theoretical result for the grain size dependence of \( \langle K \rangle \) assuming the material parameters of optimized nanocrystalline Fe–Si–B–Nb–Cu alloys [24]. We have included the contribution of the random atomic scale anisotropy of the amorphous matrix as well as the case of a small uniform anisotropy \( K_u \).

In the absence of long-range anisotropies the average anisotropy \( \langle K \rangle \) scales with \( D^6 \) down to grain sizes of about 5 nm. In this regime, where the contribution of the nanocrystallites is dominant, the expression for \( \langle K \rangle \) simplifies dramatically, i.e.

\[
\langle K \rangle := \beta \langle K_i \rangle = \beta K_u \cdot x_{\text{cr}}^2 (D/L_0)^6
\]  \( \text{(9)} \)

This result corresponds to exchange coupled crystallites diluted in an ideally soft magnetic matrix. The only modification compared with a single phase system is that the relations involve the crystalline volume fraction \( x_{\text{cr}} \).

Although the atomic scale anisotropy of the amorphous phase may be almost two orders of magnitude higher than that of the bcc crystallites its average contribution is virtually negligible, since the structural anisotropies fluctuate on the much shorter scale of atomic distances \( D_{\text{am}} \approx 0.5 \) nm. The random anisotropy of the amorphous matrix only becomes visible for very small grains, resulting in a grain size independent anisotropy. However, the related coercivity \( (H_c \approx 0.001 \) A m\(^{-1}\)) is so small that the situation shown for the smallest grain sizes in Fig. 7 remains academic.

In real materials, whether amorphous or nanocrystalline, the minimum anisotropy is ultimately determined by long-range anisotropies. To illustrate this more realistic situation we have assumed the presence of a small uniform anisotropy \( K_u = 5 \) J m\(^{-3}\). As can be seen from Fig. 7, the average anisotropy constant \( \langle K \rangle \) is almost totally determined by \( K_u \) for grain sizes below 10–15 nm. In that case the average anisotropy is

\[
\langle K \rangle \approx K_u + \frac{1}{2} x_{\text{am}} \beta K_i \sqrt{K_u} (D/L_0)^3
\]  \( \text{(10)} \)

The most remarkable feature here is that the scaling behaviour of the random anisotropy contribution changes from a \( D^6 \) to a \( D^3 \) law. For grain sizes below about 5 nm the random fluctuations \( \delta K = \langle K \rangle - K_u \) finally again
become grain size independent due to the random anisotropy of the amorphous phase. The latter is larger than that for the case $K_u = 0$, because the maximum value for the renormalized exchange length is limited by $L_{ex} = \phi(A/K_u)^{1/2}$. As a consequence, the random anisotropies of the amorphous phase are less effectively averaged out. However, their contribution to the magnetization process remains still academic.

A very small volume fraction of a phase with high anisotropy can change the picture totally. This is illustrated in Fig. 7 assuming a 1% fraction of Fe$_2$B precipitates of 10 nm grain size. The example explains at least qualitatively the finding that Fe$_2$B precipitates can significantly deteriorate the soft magnetic properties although the grain size of the bcc crystallites remains unchanged.

### 2.2.2. Grain coupling

An important aspect specific for nanocrystalline materials is the intergranular exchange interaction. This becomes most evident from the temperature dependence of the magnetic properties [21,25]. Fig. 8 shows a typical example. In nanocrystalline materials exchange coupling between the bcc grains mainly occurs via the intergranular amorphous matrix. The latter has a much lower Curie temperature than the bcc grains [2,21]. As a consequence, intergranular coupling is largely reduced as the measuring temperature approaches the Curie temperature of the amorphous matrix $T_{am}^c$, and the soft magnetic properties degrade correspondingly. Simultaneously, the domain structure changes from wide domains to a pattern of small, irregular domains [26,27]. These features are basically reversible and, thus, are not connected with irreversible, microstructural changes during measurement.

The particular example shown in Fig. 8 reveals a small uniaxial anisotropy ($K_u \approx 6 \text{ J/m}^{-3}$) aligned transverse to the ribbon axis induced by magnetic field annealing. In the low temperature regime this induced anisotropy dominates over the averaged magneto-crystalline anisotropy, as indicated by the small remanence to saturation ratio $B_r/B_s$. However, when approaching $T_c^{am}$ the random anisotropies rapidly increase due to reduced grain coupling and control the hysteresis loop. As a consequence, the remanence to saturation ratio increases sharply around 250 °C. From a theoretical analysis of the interplay between random and uniform anisotropies we expect this transition to occur at $K_u \approx 0.5\langle K_i \rangle$ for cubic crystallites. Accordingly, the increase in $B_r/B_s$ is shifted towards higher temperatures with increasing magnitude of the induced anisotropy [27], while the temperature dependence of $H_c$, being mainly determined by the random anisotropies, essentially remains the same.

The magnetic properties above the Curie point of the amorphous phase $T_{am}^c$ indicate that grain coupling is largely but not completely interrupted above $T_{am}^c$ and persists to higher temperatures. The precise coupling mechanism for $T > T_{am}^c$ is still under discussion. Both exchange penetration through the thin, paramagnetic intergranular layer [28] and dipolar interactions [25] provide reasonable explanations for the experimental findings. In any case, the strength of the coupling decreases with increasing temperature due to a simultaneous decrease in magnetization in the bcc grains. Consequently, the soft magnetic properties continue to be degraded even above $T_{am}^c$, until thermal energy dominates and the system becomes superparamagnetic.

The temperature dependence of the magnetic properties demonstrates that it is important to maintain an efficient exchange coupling between the grains by appropriate alloy design such that the Curie temperature of the residual amorphous matrix is clearly higher than the application temperature. For example, too high additions of Nb (or comparable elements), although favourable for grain refinement, can be disadvantageous because they considerably decrease the Curie temperature of the matrix [29]. Similarly, reduced grain coupling due to a low Curie temperature of the intergranular phase also provides one of the explanations for the minor soft magnetic properties of nanocrystalline Fe–Zr–B alloys [30].

### 2.3. Soft magnetic properties

For pure random anisotropies averaged out by exchange interaction the coercivity $H_c$ and initial permeability $\mu_i$ are directly related to the average anisotropy constant $\langle K \rangle$ by

$$H_c = p_s \langle K \rangle / J_s$$

$$\mu_i = p_p J_s^2 / \mu_0 \langle K \rangle$$

respectively, where $J_s$ is the average saturation polarization of the material, $p_s$ and $p_p$ are dimensionless pre-factors of the order of unity and $\mu_0$ is the vacuum permeability. These
relations were originally derived for coherent magnetization rotation in conventional fine particle systems [31]. In the regime $D < L_{\text{ex}}$, however, they also apply for domain wall displacements [12]. Accordingly, coercivity and permeability are expected to vary with grain size as $H_c \propto D^6$ and $\mu \propto 1/D^6$.

Fig. 9 shows the coercivity $H_c$ and the initial permeability $\mu_i$ of various nanocrystallized alloys as a function of the grain size $D$ [32]. The relatively broad scatter of the data is mainly related to the circumstance that experimental variations in grain size cannot be performed in a straightforward manner. It inevitably requires variations in the alloy composition and/or the annealing conditions, which both change the volume fraction and composition of the precipitated crystallites and the residual matrix. As a consequence, the local magneto-crystalline anisotropy constant $K_1$ and the exchange interaction $A$ between the grains change simultaneously. Nonetheless, the $D^6$ dependence predicted by the random anisotropy model seems to provide a good guiding principle for most of the coercivity and permeability data for grains smaller than $L_0 \approx 40$ nm. However, there are also systematic deviations from the simple $D^6$ law, in particular for small grain sizes. The major reasons are (i) precipitates of highly anisotropic compounds like Fe$_2$B and/or (ii) more long-range anisotropy contributions that are uniform on a scale much larger than the exchange length.

In particular, long-range anisotropies lead to a modified or no grain size dependence for small grain sizes. They are equally important in amorphous and optimized nanocrystalline materials. Relevant to this are magneto-elastic anisotropies, annealing-induced anisotropies and/or shape anisotropies which control the magnetization process when the random magneto-crystalline anisotropy is sufficiently averaged out.

If the magnetization process is controlled by long-range anisotropies the theoretical description of $H_c$ and $\mu_i$ becomes more complex, similar to the case in conventional soft magnetic materials. For domain wall displacements the coercivity is then determined by anisotropy fluctuations $\delta K$ according to

$$H_c = \frac{1}{\Sigma_j} \left| \frac{\partial J}{\partial K} \right|_{\text{max}} \approx \delta K L_{\text{ex}} \frac{J_s}{l_k}$$

(12)

where $\gamma_w = 4(A/K)^{1/2}$ is the domain wall energy, $L_{\text{ex}}$ is the exchange length as introduced in Eq. (8) and $l_k$ is the fluctuation length of the effective anisotropy.

For large grains $D > L_{\text{ex}}$ we have $l_k \approx D$ and $\delta K \approx K_1$, such that Eq. (12) yields $H_c \propto K_1^{1/2}/D$, i.e. the well-known $1/D$ dependence of coercivity in conventional soft magnetic materials.

In the regime $D < L_{\text{ex}}$ the wavelength of the random anisotropy fluctuations is given by the exchange length itself, i.e. $l_k \approx L_{\text{ex}}$, and the fluctuation amplitude is $\delta K = \langle K \rangle - K_0$. The coercivity is $H_c \propto \delta K / J_s$. According to Fig. 7 we thus expect that the grain size dependence of $H_c$ reveals a transition from a $D^6$ to a $D^3$ law as $K_0$ starts to dominate. Such a $D^3$ variation of coercivity has indeed been observed by Suzuki et al. [33,34] in nanocrystalline Fe–Zr–B–(Cu) alloys with grain sizes $D \approx 12–18$ nm.

The discussion has so far assumed that the long-range anisotropies are perfectly uniform. In reality, however, this assumption is often the exception rather than the rule, mostly due to internal mechanical stresses and/or surface defects. The typical fluctuation wavelengths $l_k$ are much larger than $L_{\text{ex}}$ and range from a few microns up to some 100 $\mu$m. Such $K_0$ fluctuations ultimately provide the limiting factor for the soft magnetic properties in both amorphous and optimized nanocrystalline alloys. The result is a grain size independent coercivity $H_c \propto K_0^{1/2}/l_k$, which finally dominates over the contribution of the random local anisotropies. This is the situation in amorphous alloys and in optimized nanocrystalline Fe–Cu–Nb–Si–B alloys for grain sizes below about 15–20 nm (cf. Figs. 5 and 9).

The permeability $\mu$ behaviour is even more complex when dealing with a dominant long-range anisotropy $K_0$. In particular, $\mu$ depends sensitively on the angle between the applied magnetic field and macroscopic anisotropy direction. If the sample is magnetized perpendicular to the $K_0$ axis $\mu$ is determined by magnetization rotation and, hence, is inversely proportional to the total anisotropy, i.e. $\mu \propto 1/\langle K \rangle$. It is thus grain size independent, although coercivity may simultaneously vary

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**Fig. 9.** Coercivity $H_c$ and initial permeability $\mu_i$ of the alloys versus the average grain size. The open circle corresponds to an “overannealed” Fe$_{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ alloy with a small fraction (less than 10%) of Fe$_2$B precipitates. References to the symbols are given in Fig. 5. (After Herzer [32].)
proportionally with $D^3$. If magnetized parallel to the uniform anisotropy axis $\mu$ is determined by domain wall pinning. We then expect permeability to again vary inversely with $H_c$, i.e. $\mu \propto 1/\delta K$.

Fig. 10 shows some characteristic examples for the interplay of random and uniaxial anisotropy and their consequences on the magnetization process in amorphous and nanocrystalline soft magnetic materials [27]. The examples all show the typical features expected for transverse uniaxial anisotropy, i.e. essentially linear hysteresis loops up to ferromagnetic saturation with a low remanence to saturation ratio and a permeability $\mu$ determined by the macroscopic anisotropy constant $K_u$. The domain patterns reveal wide transverse slab domains and magnetization rotation as the prevailing magnetization process. However, while the magnetization process of the amorphous sample (Fig. 10a) and the nanocrystalline sample with strong $K_u$ (Fig. 10b) is dominated by homogeneous magnetization rotation, the nanocrystalline sample with weak $K_u$ (Fig. 10c) reveals inhomogeneous magnetization rotation accompanied by domain nucleation and domain splitting. The inhomogeneous processes appear to have their origin in magnetization patches fluctuating on the scale of a few micrometres, i.e. of the order of the exchange length $L_{ex}$. These fluctuations are most pronounced in the nanocrystalline sample with low $K_u$ and are virtually invisible in the amorphous case. The more complex domain structure is also manifested in a slightly enhanced remanence to saturation ratio. These features are a consequence of the residual random magneto-crystalline anisotropy. Indeed, if the induced anisotropy of the nanocrystalline alloy is reduced further, below about 2–3 J m$^{-3}$, the remanence increases rapidly and the hysteresis loop becomes nonlinear. In comparison, the amorphous alloy still shows a low remanence and a linear hysteresis loop at an even smaller induced anisotropy of a few tenths of Joules per cubic metre, indicating a virtually negligible random anisotropy contribution.

Finally, an important point to stress is that suppression of the random magneto-crystalline anisotropy by exchange interaction works over a wide range almost independent of temperature. The situation is significantly different in highly permeable crystalline materials, like permalloys, where the magneto-crystalline anisotropy constant $K_1$ is adjusted to zero mainly by alloy composition. This adjustment is effective only for a certain temperature. Thus, as shown in Fig. 11, the temperature dependence of $K_1$ yields a pronounced variation in the soft magnetic properties around the temperature at which $K_1 = 0$ [35]. In particular, the drop in permeability at lower temperatures (at $K_1 > 0$) can be a problem for practical application. In comparison, the soft magnetic properties in amorphous and nanocrystalline materials vary more smoothly. In amorphous alloys the behaviour is mainly determined by induced anisotropies whose magnitude decreases monotonically and, thus, the permeability typically increases with increasing temperature. This mechanism also applies for nanocrystalline materials, but is opposed by the reduction in intergranular coupling at higher temperatures. Accordingly, the permeability reaches through a maximum at an intermediate temperature $T_{max}$. The latter depends on the details of the annealing conditions as well as on the alloy composition, although the physical mechanisms are still under investigation. The permeability may thus be found to increase, to decrease or even to be largely temperature independent over the range of application temperatures.

![Fig. 10. Quasi-static hysteresis loop and domain patterns (remanent state) of (a) amorphous Co$_{68}$Fe$_{8}$Mo$_{2}$Si$_{16}$B$_{10}$ ($K_u = 0.6$ J m$^{-3}$) and (b, c) nanocrystalline Fe$_{73.5}$Cu$_{3.5}$Nb$_{3}$Si$_{15.5}$B$_{7}$ with strong ($K_u = 30$ J m$^{-3}$) and weak induced anisotropy ($K_u = 3$ J m$^{-3}$). (After Flohrer [27].) |
3. Alloy systems and basic properties

The range of compositions which can be prepared in the glassy state by rapid solidification from the melt is wide. Typical compositions are given by the formula T70–90X10–30 (at.%). Here T designates a practically arbitrary combination of transition metals, which for magnetic applications are of course Fe, Co and Ni. X refers to metallic or refractory metals like Nb, Mo, Zr, Hf, etc. These “non-magnetic” additions are necessary for glass formation and in order to stabilize the amorphous structure.

The most common compositions for soft magnetic applications in either the amorphous or nanocrystalline states are metal–metalloid based (Fe, Co, Ni)–(Si,B) alloys with small additions of Mn, Nb, C and, for the nanocrystalline case, Cu. This alloy system has good glass forming ability and is easily produced on a large scale by rapid solidification as a thin ribbon. The final alloy design is largely determined by (i) the desired magnetic properties, (ii) the requirement for good glass forming ability, (iii) thermal stability and, for the nanocrystalline alloys, (iv) a well-defined crystallization behaviour.

Alloy compositions with low or no magnetostriction are of particular importance in order to achieve the highest permeability and lowest coercivity. Owing to their random structure the magnetostriction of amorphous and optimized nanocrystalline alloys is isotropic and can be characterized by a single coefficient, the saturation magnetostriction constant $\lambda_s$. The magneto-elastic anisotropy energy density is hence given by

$$\phi_e = -\frac{3}{2} \lambda_s \sum_{ij} \sigma_{ij} m_i m_j$$  \hspace{1cm} (13)

Here $m_i$ ($i, j = x, y, z$) are the components of the normalized magnetization vector and $\sigma_{ij}$ is the stress tensor. Mechanical stresses are introduced, for example, during the casting process and when winding the ribbons into toroidal cores (the major form of application). They are typically in the order of $\sigma \approx 100$ MPa. Thus optimization of the magnetic properties first requires a stress relief annealing treatment. However, a small percentage of these stresses remain even after the stress relief treatment, and additional stresses may occur from handling and housing the magnetic cores. In highly magnetostrictive Fe-based alloys ($\lambda_s \approx 30$ ppm) the associated magnetic anisotropy can be as large as $K_s = 3/2 |\lambda_s| \approx 50–100$ J m$^{-3}$ even in the stress relieved state. This limits the initial permeability to maximum values of the order of $\mu_i \approx 10,000$. Accordingly, the highest initial permeabilities of 100,000 or more can only be achieved by considerably reducing the magnetostriction constant.

3.1. Amorphous alloys

Fig. 12 summarizes the variation in the saturation polarization $J_s$ and the saturation magnetostriction constant $\lambda_s$ of amorphous alloys as a function of the Fe, Co and Ni concentrations.

The saturation polarization $J_s$ is highest in the Fe-rich alloys and decreases with increasing Ni and Co content. It is generally lower than in crystalline alloys due to the addition of non-magnetic Si and B necessary for glass formation. The $J_s$ maximum observed for crystalline Fe–Co alloys is only weakly developed and shifted to the Fe-rich side.

For the Fe-rich alloys the saturation magnetostriction $\lambda_s$ is positive, typically $\lambda_s \approx 20–40$ ppm, while for the Co-rich alloys $\lambda_s$ is negative, typically $\lambda_s \approx -5$ to $-3$ ppm. Near zero magnetostrictive compositions can be found on the Co-rich side of Co–Fe [36] or Co–Mn [37] based systems at small iron and/or manganese concentrations of about 3–8 at.%. The decrease in $\lambda_s$ with increasing Ni content is correlated with a simultaneous decrease in the saturation polarisation ($|\lambda_s| \propto J_s^2$). Thus the apparent disappearance of $\lambda_s$ at high Ni contents only occurs because the system becomes paramagnetic.

Amorphous materials are commonly divided into two major groups according to their magnetostriction: the Fe-based and Co-based alloys. The Fe-based amorphous alloys are based on inexpensive raw materials, have a high saturation magnetization but their magnetostriction largely limits their soft magnetic behaviour. On the other hand, Co-based amorphous alloys with small additions of Fe or Mn reveal nearly zero magnetostriction. Accordingly, they can offer superior soft magnetic behaviour, but their saturation magnetization is considerably lower than that of Fe-based materials.

Apart from the metallic components, the magnetic properties are also significantly determined by the metalloid content. The effect is minor in Fe-based alloys, but very pronounced in Co-based systems. Fig. 13 gives an example for near zero magnetostrictive Co-based alloys [38]. A saturation polarization of up to 1.2 T can be achieved in
Co-based alloys by reducing the metalloid content below about 20 at.%. However, these high $J_s$ alloys are close to the boundary of glass formation and reveal a relatively low crystallization temperature $T_x$, which at the same time diminishes the thermal stability of the magnetic properties.

### 3.2. Nanocrystalline alloys

A typical nanocrystalline structure with good soft magnetic properties occurs if the amorphous state is crystallized by the primary crystallization of bcc Fe, before intermetallic phases such as Fe–B compounds are formed. Both an extremely high nucleation rate and slow growth of the crystalline precipitates are needed in order to obtain a nanoscale microstructure. Such crystallization characteristics seem to be the exception rather than the rule and can be only obtained with appropriate alloy design.

The optimum alloy composition originally proposed [11] and subsequently little changed is Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ (at.%), which can be considered a typical Fe–Si–B metallic glass composition with small additions of Cu and Nb (or other group IV–VI elements). The combined addition of Cu and Nb is responsible for the formation of the particular nanocrystalline structure: copper enhances the nucleation of the bcc grains while niobium impedes coarsening and, at the same time, inhibits the formation of boride compounds.

**Fig. 12.** Saturation magnetostriction $\lambda_s$ (full lines) and saturation magnetization $J_s$ (dashed lines) in amorphous Fe–Ni-based and Fe–Co-based alloys. (After Boll et al. [10] and references therein.)

**Fig. 13.** Saturation magnetization $J_s$, Curie temperature $T_c$, and crystallization temperature $T_x$ of near-zero magnetostrictive Co-based alloys vs. the total metalloid content [38].
embedded in a residual amorphous matrix which occupies about 20–30% of the volume and separates the crystallites at a distance of about 1–2 nm [21,25]. These features are the basis for the excellent soft magnetic properties indicated by the high initial permeability values of about $10^5$ and correspondingly low coercivity of less than 1 A m$^{-1}$.

The magnetic properties and underlying microstructure are rather insensitive to the precise annealing conditions over a wide range of annealing temperatures $T_a$ of about $\Delta T_a \approx 50–100$ °C. They develop in a relatively short period of time (about 10–15 min) and do not alter much even after prolonged heat treatment of several hours. Only annealing at more elevated temperatures above about 600 °C leads to the precipitation of small fractions of boride compounds like Fe$_5$B or Fe$_2$B with typical dimensions of 50–100 nm, while the ultrafine grain structure of bcc Fe–Si persists. Annealing temperatures above about 700 °C result in grain coarsening. Both the formation of Fe borides and grain coarsening significantly degrade the soft magnetic properties.

The small grain size in the alloy Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ or similar alloy compositions is decisive in the suppression of magneto-crystalline anisotropy. However, this is only one prerequisite for superior soft magnetic behaviour. The actual highlight of nanocrystalline Fe-based alloys is that the phases formed on crystallization can simultaneously lead to low or even zero saturation magnetostriction $\lambda_s$. It is the decrease in $\lambda_s$ which is ultimately responsible for the simultaneous increase in initial permeability upon nanocrystallization. Otherwise the soft magnetic properties would only be comparable with those of stress-relieved amorphous Fe-based alloys.

Fig. 14 shows the saturation magnetostriction constant as a function of the Si content. While $\lambda_s$ is fairly independent of the composition in the amorphous state, it depends sensitively on the Si content in the nanocrystalline state. Zero magnetostriction occurs at low Si concentrations in Fe–Zr–B alloys [14,15] and at high Si concentrations of around 16 at.% in the Fe–Cu–Nb–Si–B system. The composition dependence essentially reflects the compositional variation in $\lambda_s$ found for polycrystalline $\alpha$-Fe$_{100-x}$Si$_x$ (cf. Yamamoto [39]). The detailed behaviour can be understood from the balance of magnetostriction among the structural phases present in the nanocrystalline state [40]

$$\lambda_s \approx x_{FeSi} \cdot \lambda_{FeSi}^am + (1 - x_{FeSi}) \cdot \lambda_{FeSi}^am$$

(14)

where $\lambda_{FeSi}^am$ and $\lambda_{FeSi}^am$ denote the local magnetostriction constants of the $\alpha$-Fe–Si grains and the residual amorphous matrix, respectively, and $x_{FeSi}$ is the volume fraction of the crystalline phase. Thus, near zero magnetostriction in nanocrystalline Fe-based alloys requires a large crystalline volume fraction with negative magnetostriction in order to compensate for the high positive value of the amorphous Fe-based matrix. This is achieved with pure $\alpha$-Fe ($\lambda_{FeSi}^am \approx -4 \times 10^{-6}$) in Fe–Zr–B alloys or by a high Si content in the bcc grains ($\lambda_{FeSi}^am \approx -6 \times 10^{-6}$ for $\alpha$-Fe$_{80}$Si$_{20}$) in the Fe–Cu–Nb–Si–B system.

An important point to stress is that compensation of the local magnetostriction constants to zero results in stress insensitivity of the magnetic properties, as in amorphous Co(Fe)-based alloys. This is again a consequence of the smoothing effect of the exchange interaction for structural correlation lengths much smaller than the domain wall width. Accordingly, the nano-scale fluctuations in magneto-elastic anisotropy associated with the locally varying magnetostriction constants are randomly averaged out, which results in a single isotropic magnetostriction...
coefficient. The situation thus contrasts with that for large
gained crystalline systems, where an average zero saturation
magnetostriction generally does not imply stress insen-
sitivity of the hysteresis loop. A small grain size is therefore
also a decisive factor for magnetostriction. Although it
does not directly influence the value of $\lambda_s$, it opens up a
new way to achieve isotropically low magnetostriction by
combining the properties of different structural phases with
the help of exchange interactions.

The best soft magnetic properties are found for the ori-
iginal compositions around Fe$_{70}$Cu$_{1}$Nb$_{5}$Si$_{13}$-16B$_{6-9}$ and are
comparable with the excellent properties known for per-
malloys or Co-based amorphous alloys. The advantage,
however, is the higher saturation polarization of 1.2–
1.3 T, which is twice the value of $J_\text{s}$ of near zero magneto-
strictive Co-based amorphous alloys with a comparably
high permeability level.

A major driving force in the search for further alloy
compositions has been to increase the saturation magnetiza-
tion towards the value of pure $\alpha$-Fe while maintaining
near zero magnetostriction. The major hindrance to pro-
ducing such high iron content alloys is the requirement
for good glass forming ability. Thus the Si content in
Fe–Cu–Nb–Si–B alloys cannot simply be reduced without
substitution with other glass formers. A relatively low B
content is a further requirement in order to inhibit the
formation of Fe–B compounds, which would adversely
affect the soft magnetic properties.

An efficient way to expand the glass forming range
towards low Si and B concentrations is to add refractory
metals with large atoms and low $d$-electron concentrations,
i.e. Zr, Hf, Nb and Ta. In this way a second family of near
zero magnetostrictive, nanocrystalline alloys has been
established based on Fe$_{83.3-84.3}$Si$_{4}$B$_{8}$P$_{3-4}$Cu$_{0.7}$, which
optima achieved the desired crystallization behav-
iour by the simultaneous addition of P and Cu. The optim-
ized compositions are Fe$_{51.3-54.8}$Si$_{7}$B$_{2}$P$_{1.4}$Cu$_{0.7}$, which
form ductile ribbons in the as-cast state. The authors
reported remarkably high values for saturation induction of
$B_s = 1.88–1.94$ T combined with a low coercivity of
$H_c = 7–10$ A m$^{-1}$ and low magnetostriction of $\lambda_s = 2–
3$ ppm.

These new Fe-rich alloys represent a most interesting
development. They can be produced by conventional cast-
ing technologies under an ambient atmosphere, although
the casting process may still have to be optimized to take
account of the reduced glass forming ability. Further develop-
ment also needs to address the annealing conditions,
which are more critical than for the well-established
Fe$_{51.3-54.8}$Si$_{7}$B$_{2}$P$_{1.4}$Cu$_{0.7}$ alloys. In order to achieve optimum
soft magnetic properties the new alloys require relatively
short annealing times of only 5–10 min, thus rather high
heating rates of 200–400 K min$^{-1}$ are needed to reach the
annealing temperature [42,43].

4. Annealing-induced anisotropies

So far magnetic anisotropy has been discussed as a dis-
ruptive factor with respect to soft magnetic properties.
However, if properly controlled it can also be a powerful
tool in tailoring the shape of the hysteresis loop according
to the demands of various applications. In both amorphous
and nanocrystalline materials this can be realized by either
either magnetic field annealing or tensile stress annealing,
both of which yield uniform uniaxial anisotropy. Magnetic field
annealing is of particular importance.

Magnetic field annealing induces uniaxial anisotropy
with an easy axis parallel to the direction of the magnetic
field applied during the heat treatment. Anisotropy forma-
tion is related to directional atomic ordering along the
direction of the local magnetization in order to minimize
the spin orbit coupling energy [44,45]. Fig. 16 shows some
typical examples of hysteresis loops and the corresponding
impedance permeability obtained after different heat
treatments.

The flat loops (F1, F2) are obtained by transverse field
annealing, i.e. by inducing a uniaxial anisotropy perpen-
dicular to the ribbon axis. The magnetization process is deter-
mined by rotation of the magnetization vectors from the
easy axis towards the ribbon direction. This results in a per-
meability $\mu$ practically constant up to ferromagnetic satu-
ratation, which is directly related to the induced anisotropy
energy constant $K_u$ by

$$\mu = \frac{J_s^2}{2\mu_0 K_u}$$ (15)
This flat loop shape has the most reproducible properties, lowest losses (cf. Fig. 2 and dashed line in Fig. 7) and, hence, is of particular importance for the application of amorphous and nanocrystalline materials.

The rectangular loop (Z) results after longitudinal field annealing. The uniaxial anisotropy is parallel to the ribbon axis. The magnetization process is dominated by 180° domain wall displacements. The highest maximum permeabilities can be achieved in this way. Although the strength of the induced anisotropy is not directly evident from the shape of a rectangular loop, it has a significant effect on the dynamic magnetization behaviour. As an example, Fig. 17 shows the power loss of various amorphous and nanocrystalline alloys as a function of the induced anisotropy constant $K_u$.

Portional to the square root of $K_u$, fewer domain walls will be generated with increasing $K_u$. This increases the localization effect and, hence, the magnitude of the excess losses. Low induced anisotropies, however, facilitate domain refinement, which reduces these excess eddy current losses [46,47].

The round loop (R) results after conventional annealing without application of a magnetic field. The magnetization process is a mixture of magnetization rotation and domain wall displacement. Characteristic features of the round loop are a high initial and high maximum permeability. However, annealing without application of a magnetic field does not mean that there are no induced anisotropies. The latter are always induced along the local direction of spontaneous magnetization within a ferromagnetic domain as long as the annealing temperature is lower than the Curie temperature. One should therefore more precisely speak of magnetization-induced instead of field-induced anisotropies. Application of a magnetic field during annealing merely aligns the magnetization, which leads to uniform anisotropy. Correspondingly, zero field annealing yields a distribution of uniaxial anisotropies reflecting the domain structure during heat treatment. The remanence to saturation ratio of around 50%, typical for randomly oriented uniaxial anisotropies, indicates that these randomly induced anisotropies are fluctuating on a scale larger than the exchange length and, hence, control the soft magnetic properties at small grain sizes. Rotating field annealing, which results in a significantly reduced coercivity and enhanced remanence [48,49], can reduce these induced anisotropy fluctuations. Similarly, field annealed samples also reveal a smaller coercivity than samples annealed without a field. This can be understood from the less complex domain configuration due to the homogeneously induced anisotropy. Correspondingly, proper transverse field annealing allows a higher initial permeability than that obtained by conventional heat treatment without a magnetic field.

Fig. 16. DC hysteresis loops and 50 Hz permeability of nanocrystalline Fe$_{73.5}$Cu$_{1}$Nb$_{3}$Si$_{13.5}$B$_{9}$ annealed for 1 h at 540 °C without (R) and with a magnetic field applied parallel (Z) and transversely (F2) ($K_u \approx 20$ J m$^{-3}$, $\mu \approx 30 \times 10^4$) to the magnetic path. Sample F1 ($K_u \approx 6$ J m$^{-3}$, $\mu \approx 100 \times 10^4$) was first crystallized at 540 °C and subsequently transverse field annealed at 350 °C. (Reprinted from Herzer [2]).

Fig. 17. Power loss of amorphous and nanocrystalline materials with square loop (solid symbols and full line) and flat loop (open symbols and dashed line), respectively, as a function of the induced anisotropy constant $K_u$. 
The almost perfectly rectangular or flat hysteresis loops after field annealing indicate that field-induced anisotropy clearly dominates over the residual contributions from magneto-crystalline and magneto-elastic anisotropies. The induced anisotropy constant $K_u$ can be made small enough to achieve the highest permeabilities (for example $\mu \approx 200,000$, as for the amorphous and nanocrystalline sample shown in Fig. 10).

The magnitude of $K_u$ depends upon the alloy composition and the annealing conditions [45]. The characteristic features of anisotropy formation are shown in Fig. 18 and can be summarized as follows. (i) Anisotropy only occurs on annealing below the Curie temperature $T_c$ since the driving forces are magnetic interactions. The equilibrium value of $K_u$ achieved after an infinite annealing time approximately scales with the square of the saturation magnetization at a given annealing temperature. (ii) Anisotropy formation is governed by thermal activation. At lower annealing temperatures the kinetics are too slow to reach the equilibrium value which results in a typical maximum of $K_u$ at a certain annealing temperature. (iii) Alloys with two or more different kinds of magnetic metallic elements show considerably stronger field-induced anisotropies than amorphous alloys with only one transition element.

In principal any level of $K_u$ can be produced by appropriate choice of the annealing temperature and time. The annealing conditions which can be realized in practice, however, only allow $K_u$ variation by about a factor of 3–5 around the maximum value of the $K_u$ vs. $T_a$ curve shown in Fig. 18. The latter is determined by the alloy composition. Accordingly, low values of $K_u$, i.e. high permeabilities, can only be achieved in alloys with one magnetic transition metal and, possibly, a low Curie temperature.

The situation is similar in nanocrystalline materials. If the material is first nanocrystallized without an applied field and subsequently field annealed at lower temperatures the resulting $K_u$ depends on the annealing temperature $T_a$ and time $t_a$ (cf. Fig. 19a). However, the kinetics are considerably slower [50] than in the amorphous case, which shifts the maximum of the $K_u$ vs. $T_a$ curve to considerably higher annealing temperatures. This allows tailoring of the lowest induced anisotropies, i.e. highest permeabilities, but with significantly better thermal stability than in amorphous alloys or even in permalloys.

If field annealing is performed during nanocrystallization the induced anisotropy reaches a maximum value, which is relatively insensitive to the precise annealing conditions and thus corresponds to the equilibrium value characteristic for the alloy composition [51].

The Curie temperature of bcc grains ranges from about $T_c = 600$ to $750$ °C (depending on composition) and is considerably higher than the $T_c$ of the amorphous matrix (200–400 °C) [2]. Thus the anisotropy induced by a magnetic field applied during nanocrystallization primarily originates from the bcc grains. Accordingly, the induced anisotropy in nanocrystalline Fe–Cu–Nb–Si–B alloys is mainly determined by the Si content and the fraction of bcc grains $x_{cr}$. The dependence of $K_u/x_{cr}$ on the Si content in bcc grains (Fig. 19b) is comparable with that observed for conventional α-FeSi single crystals [52], in which the formation of field-induced anisotropy has been proposed to arise from the directional ordering of Si atom pairs.

The decrease in $K_u$ with increasing Si content can be related, in terms of Néel’s theory [44], to the formation of a DO3 superlattice structure for Si concentrations above about 10 at.%; for completely ordered Fe2Si the lattice sites for the Fe and Si atoms are entirely determined by chemical interactions, allowing no degree of freedom for an orientational order. However, for the composition $\text{Fe}_{1-x}\text{Si}_x$ with less than 25 at.% Si no complete DO3 order can be reached and Fe atoms will occupy the vacant sites in the Si sublattice. The way the latter occurs provides the necessary degrees of freedom for orientational ordering. Thus the present anisotropy data above about 10 at.% Si can be described by (see dashed line in Fig. 19b) [53]

$$K_u/x_{cr} = K_0 c^2 (1 - c^2)$$

where $c = (1-4y)$ denotes the fractional concentration of Fe at Si sites. The low $K_u$ value due to the superlattice
structure at higher Si contents is an additional key factor for high initial permeabilities, which can be achieved in these alloys despite their high Curie temperatures and their high saturation induction.

For low Si contents the situation is more complex and still under investigation. Pure $\alpha$-Fe should reveal no field-induced anisotropy, in accordance with the decrease in $K_u$ reported for $\alpha$-FeSi single crystals with low Si contents [52]. However, nanocrystalline alloys still show a considerable amount of induced anisotropy at negligible Si contents. A recent analysis [49] indicated that this unexpected anisotropy might be due (i) to a contribution from the amorphous matrix and (ii) to the fact that the crystallites do not consist of pure $\alpha$-Fe but contain a small amount of B, revealing directional ordering eventually stabilized by a local tetragonal distortion to bct. The presence of high $T_c$ phases, such as Fe$_2$B ($T_c \approx 550 \, ^\circ C$) or Fe$_2$B ($T_c \approx 740 \, ^\circ C$) compounds, may also contribute significantly to $K_u$ [2]. The precise mechanism needs further investigation. Thus stabilizing an intrinsically low $K_u$ value in Fe-rich nanocrystalline alloys by means of alloying is a highly demanding challenge for future alloy development.

Fig. 20 compares the permeability of transverse field annealed amorphous and nanocrystalline materials as a function of the saturation polarization with other low $K_i$ and low $\lambda_4$ alloys. For amorphous alloys the highest permeabilities of $\mu_i > 10^5$ can only be obtained in Co-based alloys with $J_s < 0.6 \, T$ due to their low Curie temperature of $T_c < 250 \, ^\circ C$. In comparison, nanocrystalline materials exhibit much higher permeabilities, despite their high saturation polarizations and high Curie temperatures.

The tremendous practical impact of field-induced anisotropies is almost self-evident. Their understanding is key to the reproducible control of soft magnetic properties according to the demands of various applications. This not only holds for the magnetic properties achieved after annealing but also for their thermal stability at the application temperature. Thus the mechanisms of thermal ageing are, in principle, the same as those that tailor the magnetic properties during annealing. Good thermal stability of the magnetic properties, therefore, also requires a possibly high activation energy and slow kinetics of anisotropy formation.

Empirically, thermally induced ageing of the magnetic properties is more critical the better these properties are. Apart from temperature and time, the ageing behaviour also depends on the magnetizing conditions during operation, whose limiting cases are the remanent (or demagnetized) state and the ferromagnetically saturated state, respectively. The latter generally represents the worst case. Fig. 21 compares the ageing behaviour of a highly permeable amorphous Co-based alloy, nanocrystalline Fe$_{73.5}$Cu$_1$Nb$_{13.5}$Si$_{15.5}$B$_7$ and crystalline Ni–Fe. Thermal ageing is a particular problem for highly permeable Co-based alloys and limits the upper continuous service temperature to about 80–100 $^\circ C$. In comparison, the thermal stability of the nanocrystalline material surpasses by far that of amorphous alloys and even that of permalloys. This allows higher continuous service temperatures of up to about 150 $^\circ C$.

Fig. 19. Field-induced anisotropy $K_u$ in nanocrystalline Fe–Cu–Nb–Si–B alloys. (a) Influence of the annealing conditions and (b) role of the composition in the nanocrystalline state. The dashed line in (b) is a fit according to Eq. (16) with $K_u = 612 \, J \, m^{-3}$. (After Herzer [2].)

Fig. 20. Initial permeability vs. saturation polarization for low magnetostrictive, soft magnetic materials. (After Herzer [2].)
The excellent thermal stability of the magnetic properties is a further highlight of soft magnetic nanocrystalline alloys and is closely related to the factors governing anisotropy formation discussed above. Thus the reduced degrees of freedom for anisotropy formation due to the superlattice structure together with the high Curie temperature allows stabilization of very small induced anisotropies and, hence, high permeabilities at annealing temperatures much higher than possible for highly permeable amorphous alloys or permalloys. This essentially reduces the kinetics of anisotropy changes at the application temperature. In comparison with amorphous metals, the thermal stability is additionally improved by the more stable crystalline structure.

5. Conclusions

The key to the properties of both amorphous and nanocrystalline soft magnetic alloys is that the structural correlation length is much smaller than the ferromagnetic correlation length. Thus the magneto-crystalline anisotropy is randomly averaged out by exchange interactions. In nanocrystalline systems this averaging effect of exchange interactions in the small grain size regime allows combination of the individual properties of different structural phases. A particular highlight is the low magnetostriction achieved in this new way for certain alloy compositions.

A negligibly low magneto-crystalline anisotropy and low or no magnetostriction are the key to superior soft magnetic properties. There are only a few alloy compositions that exhibit this combination of properties: the permalloys, Sendust, manganese–zinc ferrites, amorphous cobalt-based alloys and nanocrystalline iron-based alloys. However, soft magnetic applications require not only superior soft magnetic properties in terms of high permeability and low coercivity. A well-defined shape of the hysteresis loop, with not necessarily the highest but a well defined level of permeability, is as important. This is realized by magnetic field-induced anisotropies which play an important role in tailoring the magnetic properties according to the requirements of the application.

Superior soft magnetic properties can be achieved as well in amorphous Co-based as in nanocrystalline Fe-based alloys. The advantages of nanocrystalline alloys, however, are the higher saturation induction of 1.2–1.3 T and significantly better thermal stability of the soft magnetic properties. The best soft magnetic properties are still found for compositions similar to the originally proposed one, i.e. Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{15.5}$B$_7$ (Vitroperm 800), although interesting new developments have recently been reported [41–43]. The combination of high saturation magnetization and high permeability together with good high frequency behaviour, low losses and the good thermal stability allows a reduction in the size and weight of magnetic components used in, for example, switched mode power supplies or telecommunications. Apart from that, the materials are based on the inexpensive raw materials iron and silicon. Taken together, this has made the nanocrystalline solution competitive not only with amorphous Co-based alloys but also with classical crystalline alloys and ferrites. The consequence is steadily increasing application in magnetic cores for ground fault interrupters, common mode chokes and high frequency

Fig. 21. Relative change in the initial permeability vs. the time of thermal ageing at elevated application temperatures. The comparison is made for highly permeable materials with low remanence hysteresis loops. (Reprinted from Herzer [2].)

Fig. 22. Toroidal wound cores and components of nanocrystalline Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{15.5}$B$_7$ (Vitroperm 800).
transistors. Fig. 22 shows some typical examples. The worldwide production rate meanwhile has exceeded 1000 tons per year, and is increasing. However, the variability in their soft magnetic properties as well as their form of delivery so far are still restricted compared with amorphous or other soft magnetic materials. Thus amorphous alloys may reveal good soft magnetic properties in the as-cast state or after moderate annealing. They can be delivered as a ductile product useful for, for example, flexible magnetic screening or for sensor applications, most notably in electronic article surveillance. The major drawback of nanocrystalline materials is severe embrittlement upon crystallization, which requires final shape annealing and restricts their application mainly to toroidally wound cores. However, the situation is similar for highly permeable amorphous alloys due to the need for stress relief treatment, which also causes embrittlement.

References