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# SOFT MAGNETIC NANOCRYSTALLINE ALLOYS

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During the last decade, nanocrystalline alloys have received a great interest because of their unusual structural and magnetic properties. Their soft magnetic features stimulated the fundamental research. This paper reports some general structural, microstructural and magnetic aspects of soft magnetic nanocrystalline alloys and reviews the different tools which are commonly used to characterize these alloys. The state of art in research and applications is assessed.

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## 1. Introduction

The amorphous solid state has been widely investigated in the second half of the 20$^{th}$ century, although some first ideas to model the structure of vitreous silica were proposed earlier by Zachariasen [1]. After the discovery of the metallic glasses obtained by melt-quenching techniques by Duwez et al. [2] at Caltech in 1960, an intense research activity has been devoted first to the improvement of the preparation conditions, then to the understanding of the physical properties as well as to the technological developments. Some important dates are listed in Table 1. Indeed, the metglasses display soft ferromagnetic properties combining high induction and large permeability in addition to their excellent mechanical properties and corrosion resistance, making them challenging magnetic materials. Fundamental aspects, evidenced by structural and magnetic modelling, were strongly debated.

More recently, first nanocrystalline alloys were discovered by Yoshizawa et al. [13] in 1988, giving rise to a rather similar situation. Indeed, the nanocrystalline alloys emerged at the same time as nanoparticles, multilayers, nanostructured alloys, contributing to the early state of nanosciences. One decade later, a lot of nanocrystalline systems have been extensively investigated and their physical properties were quite well established (see review papers [18-20]). However, numerous fundamental aspects remain opened and the technological development is quite limited compared to that of nanoparticles, nanodots and multilayers.

We briefly report some general aspects of the nanocrystalline alloys. The different systems are first listed including preparation aspects. The structural and magnetic properties are then presented, in conjunction with a critical review of the methods of investigation. Finally, an overview on applications is given.

## 2. The structural aspects of nanocrystalline alloys

Since most of amorphous alloys exhibit a coarse microstructure with crystalline grains of 1-10 μm after annealing at temperatures higher than the single crystallization temperature, a few

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series of amorphous alloys present two crystallization stages. The first stage of crystallization corresponds to the emergence of ultrafine crystalline grains (diameter ranged from a few nm up to 20 nm) while the complete transformation of the amorphous remainder into microcrystalline grains occurs during the second stage of crystallization. Subsequent annealing treatment (time and temperature) favours the transformation from the amorphous state into the nanocrystalline state. But it is important to mention that rather low quenching rates might produce directly the nanocrystalline state. Nevertheless, both the size and the morphology of crystalline grains are not homogeneous. In addition, such a procedure does not allow a reproducibility of the nanocrystalline state, while the subsequent annealing treatment of the amorphous precursor gives rise to the same nanocrystalline alloy, providing the amorphous states are similar.

Table 1. Important dates for amorphous state studies, amorphous and nanocrystalline metal-metalloid alloys.

| |
|---|
| Brenner, Couch, Williams (1950) electro chemical deposition Ni-P alloys [3] |
| Buckel and Hilsch (1952) sputtering $10^8$ K.s$^{-1}$ [4] |
| Gonser, Okkerse, Fujita (1958) irradiation $10^{14}$ Ks$^{-1}$ [5] |
| Duwez, Willens, Klement (1960) melt-spinning $10^6$ Ks$^{-1}$ Au-Si alloy [2] |
| Bernal (1964) Dense Random Packing of Hard Spheres [6] |
| Pond, Maddin (1969) melt-spinning Continuous ribbons [7] |
| Polk (1971) Continuous Random Network [8] |
| Gaskell (1979) Chemical Short-Range Order Model [9] |
| Gleiter (1981) nanocrystal deposition [10] |
| Yeh, Samwer, Johnson (1983) solid state reaction [11] |
| O'Handley et al (1985) first nanocrystalline state [12] |
| in a partially devitrified Co amorphous alloy |
| Yoshizawa et al (1988) FINEMET $Fe_{73.5}Cu_1Nb_3B_9Si_{13.5}$ |
| FeCuMBSi with M = Nb, Zr, V, Mo, ... [13] |
| Inoue et al (1988) Non Ferrous Bulk Amorphous Alloys $10^4$ - 1 Ks$^{-1}$ |
| Mg-Ln-M M=Ni,Cu,Zn [14] |
| Suzuki et al (1991) NANOPERM $Fe_{87}Zr_{3.5}Nb_{3.5}B_8Cu_1$ |
| FeMB(Cu) with M = Zr, Hf, Nb, ... [15] |
| Inoue et al (1992) Ferrous Bulk Amorphous Alloys $10^4$ - 1 Ks$^{-1}$ |
| Fe-(Al, Ga)-(P, C, B, Si, Ge) [16] |
| Willard et al (1998) HITPERM $Fe_{44}Co_{44}Zr_7B_4Cu_1$ |
| (Fe,Co)MBCu with M = Zr, Hf, Nb, ... [17] |

Three main families are well established up to now: the pioneering one derives from FINEMET® $Fe_{73.5}Cu_1Nb_3B_9Si_{13.5}$ discovered in Hitachi Metals Co. by Yoshizawa et al. (1988) with general composition FeCuMBSi with M = Nb, Zr, V, Mo, … [13]. Suzuki et al. (1991) first proposed the second series known under trade name NANOPERM® FeMB(Cu) with M = Zr, Hf, Nb, … where the nanocrystalline grains result from bcc Fe [15]. The compound $Fe_{84}Zr_{3.5}Nb_{3.5}B_8Cu_1$ exhibits the best magnetic properties. The last series initiated by Willard et al. (1998) concerns FeCo based alloys so called HITPERM® with composition (Fe, Co)MBCu (M = Zr, Hf, Nb, … ) [17]: the main alloy is $Fe_{44}Co_{44}Zr_7B_4Cu_1$, which is technologically promising at high temperature.

The microstructure, the chemical composition of the amorphous remainder as well as the structure, the size and the morphology of crystalline grains have been widely investigated for those different systems as a function of annealing temperature, annealing time and the composition of the

melt-spun amorphous precursor. In addition, both the kinetics and the thermodynamics were also carefully examined [see 18 and references therein]. Several techniques have to be mutually used in addition to theoretical calculations, as it is schematised in Fig. 1. It is well established that the presence of Cu favours the nucleation of clusters and thus the emergence of Fe-based nanocrystalline grains, while the presence of M atoms prevents the growth of crystalline grains up to a large scale. But it is rather important to emphasize that Cu-free amorphous precursors give also rise to the nanocrystalline state, with a distribution of both size and morphology of grains. The density of crystalline grains or the volumetric crystalline fraction is rather less sensitive to the annealing time (usually ranged from 1 s to 1 hour) than to the annealing temperature. Some relevant questions at this stage concern the structure and the chemical content of the crystalline grains (presence of impurities and content, if any), the size and morphology of crystalline grains, and their growth as a function of the atomic diffusion mechanism during the transformation from the amorphous state into the nanocrystalline state. The occurrence of an interfacial zone has been conceptually proposed on the basis of high surface/volume ratio of nanocrystalline grains and experimentally evidenced by Mössbauer spectrometry. This point has been controversially debated [21-23].

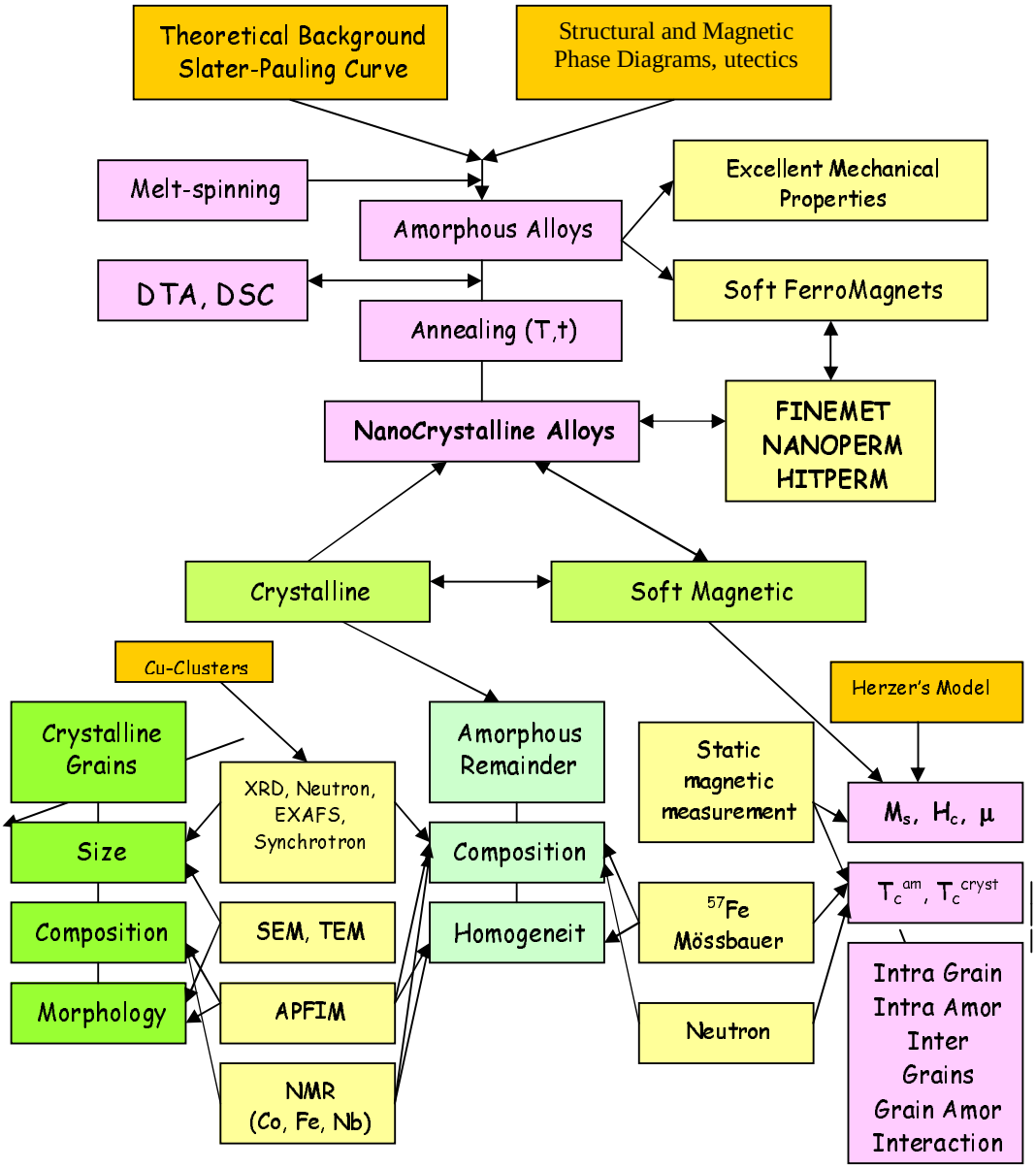


Fig. 1. Diagram showing predictions, thermodynamic considerations, processing and methods of analysis of nanocrystalline alloys.

Fe and Co atomic ordering remains also an important question in the case of HITPERM alloys. Synchrotron XRD experiments earlier revealed the presence of a superstructure Bragg peak attributed to the ordered α'-FeCo phase in the precursor HITPERM alloy, $Fe_{44}Co_{44}Zr_7B_4Cu_1$ [17]. Fe and Co partitioning in both crystalline grains and amorphous remainder has to be investigated by combining X-ray diffraction, Atom Probe Field Ion Microscopy, $^{57}$Fe Mössbauer spectrometry and $^{60}$Co NMR: such a study is in progress.

Different techniques including X-ray diffraction, XANES and EXAFS, Transmission Electron Microscopy, $^{57}$Fe Mössbauer spectrometry [19] and Atom Probe Field Ion Microscopy (APFIM) [24] have to be commonly used to get an atomic scale description of crystalline grains, and to investigate the chemical heterogeneity of the amorphous remainder. Few NMR studies were reported up to now. Therefore, extensions are especially expected in the case of HITPERM alloys. However, it is important to emphasize that all those techniques allow the volumetric crystalline fraction to be estimated, but the different results cannot be directly compared. Let us note that the analysis of diffraction patterns allows only to estimate the mean values of lattice parameters and size of nanocrystalline grains while both morphology and distribution of grain size can be deduced from electron micrographs. Hyperfine data resulting from $^{57}$Fe Mössbauer spectra which are rather complex, provide relevant information on the structural type of crystalline grains and on the different kinds of iron probe neighbourings located in the amorphous remainder. It is important to mention that the fitting procedures require great attention to avoid misinterpretations, whatever the technique is [19, 25-30]. Finally, APFIM which combines a field ion microscope and time-of-flight mass spectrometer, allows to describe the atomic structure of both crystalline and amorphous parts thanks to its single ion sensitivity. Their evolution as a function of the crystalline fraction, related to the annealing temperature, permits to establish the atomic diffusion mechanism occurring during the transformation from the amorphous state to the nanocrystalline state. The main characteristics of crystalline grains in some nanocrystalline alloys are listed in Table 2.

In the case of Cu containing FINEMET alloys, the Cu atoms first precipitate into fcc clusters below the onset of the primary crystallization which favours thus the emergence of FeSi nanocrystalline grains and their growth is limited by the presence of M atoms which progressively act as a barrier preventing the diffusion of Fe and Si into grains. It is important to emphasize that the absence of Cu atoms does favour neither a good crystallinity, nor a good morphology nor an homogeneous distribution size of crystalline grains. But it has been also showed that Cu-free alloys have the same microstructure as the 1% Cu containing alloy.

Finally, it is also important to pay attention to the transformation of the residual amorphous phase in crystalline state. The identification of the crystallization products provide relevant information on the composition of the residual amorphous phase.

Table 2. Main crystalline and magnetic characteristics of some nanocrystalline alloys.

| Alloy Trade Name | Typical composition | Nanocrystalline phase | $B_s$ (T) | $T_c$ (°C) |
|---|---|---|---|---|
| FINEMET | $Fe_{73.5}Si_{13.5}B_9Nb_3Cu$<br>$Fe_{65.5}Al_8Si_{13.5}B_9Cu_1Mo_3$<br>$Fe_{60}Co_{13.5}Si_{13.5}B_9Nb_3Cu$<br>$Fe_{13.5}Co_{60}Si_{13.5}B_9Nb_3Cu$ | α-FeSi, FeSi (DO3)<br>α-FeSiAl, FeSiAl (DO3)<br>α-FeCoSi (DO3)<br>α-FeCoSi | 1.0 - 1.2 | < 770 |
| NANOPERM | $Fe_{88}Zr_7B_4Cu$ | α-Fe(BCC) | 1.5 - 1.8 | 770 |
| HITPERM | $Fe_{44}Co_{44}Zr_7B_4Cu$ | α-FeCo (BCC)<br>α'-FeCo (B2) | 1.6 - 2.1 | > 965 |

## 3. The magnetic aspects of nanocrystalline alloys

The nanocrystalline structure favours both low effective magnetocrystalline anisotropy and low magnetostriction [5]. Consequently, these two magnetic phases systems show excellent soft magnetic properties, which are strongly dependent on the volume fraction of the crystalline phase

(size of the crystalline grains and their density, *i.e.* the intergrain distance). It is important to emphasize that this soft magnetic behaviour is only observed at rather low temperature, i.e. at room temperature, much below the Curie temperature of the amorphous remainder. Up to now, the best combination of the saturation magnetisation (~1.2 T) and high permeability (~$10^5$ at 1 kHz) is achieved at room temperature for the pioneering nanocrystalline FINEMET ($Fe_{73.5}CuNb_3Si_{13.5}B_9$). However, a rapid deterioration of these properties is observed with increasing temperature, close to the Curie point of the amorphous material. On the contrary, the HITPERM alloys seem more promising at high temperatures. Thus, the NANOPERM alloys are mainly of a fundamental interest due to their rather simple crystalline phase structure. The main magnetic characteristics are listed in Table 2.

Experimental studies have to be thus performed by means of complementary techniques: static magnetic measurements, $^{57}$Fe Mössbauer spectrometry, NMR and ferromagnetic resonance, while either theoretical calculations or computer simulations allow to predict some magnetic behaviours.

An improvement in the soft magnetic behaviour of those nanocrystalline alloys requires firstly an excellent characterisation of their structure and microstructure and then an understanding of the magnetic interactions (exchange and dipolar contributions, induced anisotropies, thermal fluctuations, …) of the crystalline grains and the intergranular phase and magnetic coupling between the crystalline grains through the intergranular phase. The low value of coercive field is well described by the Herzer's model, derived from the so-called random anisotropy model originally proposed for amorphous ferromagnets.

The effective magneto-crystalline anisotropy is essentially reduced by both the small grain size and the exchange interactions between grains. In fact, the grain size is much smaller than the ferromagnetic exchange length (minimum distance within the magnetic moments that are ferromagnetically oriented by exchange interaction) and the effective magneto-crystalline anisotropy is thus averaged out over all crystalline grains, assuming an assembly of randomly oriented grains. This gives rise to a $D^6$ dependence of the coercive field and magnetic permeability when the grain size is lower than about 40 nm. Those predictions are well supported by experimental data as obtained on nanocrystalline alloys. In addition, the coercive field increases with temperature and then reaches a maximum at about the Curie temperature of the amorphous remainder and, finally, vanishes abruptly to zero together with the remanent magnetization.

High temperature magnetic behaviour, i.e. above the Curie temperature of the amorphous remainder, is strongly dependent on the volumetric fraction of crystalline grains. Low crystalline content alloy can be described as an assembly of single domain crystalline grains with a superparamagnetic behaviour while increasing the crystalline fraction favours progressively the occurrence of interacting magnetic grains. At extremely high volumetric fraction, the corresponding system displays an heterogeneous magnetic behaviour because of the emergence of penetrating fields that polarize the intergranular magnetic phase. Such phenomena prevent to clearly define the Curie temperature of the intergranular phase, which is, in other words, distributed over a wide range of, temperatures.

## 4. Applications

Among the magnetic materials, soft ferromagnetic amorphous alloys strongly contribute to industrial technologies [31, 32]. It is well established nowadays that iron-based metallic glasses display relatively large magnetization and remain highly magnetostrictive while cobalt-based systems exhibit smaller magnetization but low magnetostrictive behaviour. Those properties combined with low hysteretic and eddy current losses, excellent mechanical hardness and highly resistant corrosive properties gave rise to several applications as included in power transformers, inductive components for switched mode power supplies, reinforcement in concrete, … [33]. Nanocrystalline ferromagnets are expected to play also a challenging role: FINEMET shows exceptional combination of low coercive field and very high permeability, in addition to extremely low magnetostriction, while high temperature good properties are achieved from HITPERM alloys. Nevertheless, the high ductility of nanocrystalline alloys due to the annealing treatment prevents those systems to be technologically

applied. However, FINEMET and NANOPERM alloys are suggested to be included in chock coils cores [34], transformer core materials and power transformers [35], respectively.

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