Characterization and processing of cobalt based nanostructured magnetic materials

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Characterization and Processing of Cobalt Based Nanostructured Magnetic Materials

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**School of Materials Science & Engineering
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Abstract

Nanostructured magnetic materials are expected to have superior magnetic properties and are useful to improve the efficiency of devices as well as to increase the range of applications, Co and Co-Fe based nanostructured magnetic alloys have not been well explored although they exhibit a number of attractive properties. This project focused on the formation of nanostructures in Co and Co-Fe based alloys using crystallization of melt spun amorphous precursors and mechanical alloying (MA) techniques, as well as characterization of the nanostructures fundamentally using DSC, electrical resistivity measurements, XRD, TEM, SEM and VSM. The alloys were chosen to be based on the compositions of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy.

The investigation of the crystallization of the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy showed for the first time a novel metastable phase comprised of highly modulated nanolamellar structure (wavelength of about 7 nm). This alloy possesses a multi-step crystallization mechanism: crystallization into large grains with nanolamellar structure $\rightarrow$ precipitation at grain boundaries and inside the grains $\rightarrow$ formation of heterogeneous microstructure $\rightarrow$ formation of equiaxed grains. The nanolamellar structure occurred within all the large grains of the first transformation event, these grains have a C base centered orthorhombic crystal structure with $a=0.74$ nm, $b=1.07$ nm and $c=0.77$ nm. The nanolamellae were modulated in the (0 0 1) plane. The mechanism of formation of the nanolamellar structure was considered to be spinodal decomposition within the grains. In situ TEM observations revealed that the crystallization was highly thickness dependent due to strain effects and enhancement of the atomic mobility in the thin foil. Coarsening of the nanolamellar structure was studied in detail for both conventional and in situ thin foil annealing, the large grains with nanolamellae eventually transformed into equiaxed grains consisting of Co_2Si , Co_2B and h.c.p Co equilibrium phases. The magnetic properties deteriorated upon crystallization.

MA of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ from elemental powders successfully yielded amorphous Co-Si-B alloys. The amorphization occurred directly without pre-formation of the crystalline alloys and it was a continuous transformation process. Addition of Fe and Ni increased the crystallization temperatures of the amorphous phase and facilitated the crystallization process. The properties of the MA amorphous Co based alloys were similar to the melt spun alloys. The magnetic properties degraded upon crystallization.

The Cu free HiTperm $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous alloy crystallized into a high density of α -(Co, Fe) nanocrystals and a secondary phase of $(\text{Co, Fe})_3\text{Zr}$ upon annealing. The primary nanocrystals, which appeared to be clustered, were found instead from TEM, HRTEM and CBED analysis, for the first time, to be single crystals formed in a compact dendritic morphology. Due to the high nucleation density and the composition difference between the nanocrystals and the remaining amorphous matrix, the growth of nanocrystals was slow when the size reached around 30 nm; significantly, this resulted in a stable nanocrystalline structure. The soft magnetic properties improved after primary crystallization and deteriorated after secondary crystallization of this alloy as expected.

MA from elemental powders also successfully yielded nanostructured Co-Fe based alloys. A banded microstructure was observed in the as milled $\text{Co}_{50}\text{Fe}_{50}$ powders, which was due to texture effects. The alloying elements P and B were found to have a strong effect on the powder size, morphology and inner microstructure, addition of them during MA of Co-Fe based alloys led to formation of spherical nanocrystals instead of banded microstructures. The as milled Co-Fe based alloy powders were not magnetically soft. Annealing significantly improved the soft magnetic properties of these alloys.

Chapter 1 Introduction

Nanotechnology has applications in every walk of life; it is almost a household word nowadays. Magnetic materials have wide applications including transformers in power electronics, sensors, magnetic field shielding and antitheft security systems; they have also increasingly been used in newer areas, such as MEMS and bioengineering. Nanostructured magnetic materials, which can have unique and improved properties, can be used to make more efficient devices and systems; new areas for research and applications are also being actively explored. In this project, an investigation of nanostructured magnetic materials was carried out. The motivation of this project, goals to be reached and routes of investigation are introduced in this chapter.

1.1 Nanomagnetic materials: Advantages

Nanotechnology is a futuristic technology that can make products light, efficient, strong and with improved functional properties. Nanomaterials refer to materials with microstructures modulated on length scales less than 100 nm [1-3]. Materials with such fine microstructures have a large fraction of atoms at surfaces and at grain boundaries; the physical, chemical, thermal, electrical, magnetic and mechanical properties of materials can be dramatically modified. E.g., nanosized metal particles can have attractive colors although conventional sized metals (except for gold and copper) can only be dark brown or black, or silvery if they have smooth surfaces.

“The principles of physics, as far as I can see, do not speak against the possibility of maneuvering things atom by atom. It is not an attempt to violate any laws; it is something, in principle, that can be done; but in practice, it has not been done because we are too big.” — Richard Feynman

The use of the word “nano” has been applied to many aspects of science and technology, such as nanoparticle, nanophase, nanomachine, nanostructure, nanocrystal,

nanoscience, etc. Nanostructures provide new opportunities for tailoring the properties of magnetic materials [4]. Nanomagnetic materials are therefore one focus area of current nanomaterials research.

The magnetic properties of materials include saturation magnetization M_s , coercivity H_c , permeability μ , Curie temperature T_c and magnetostriction λ [5, 6]. M_s and T_c are relatively structure insensitive. The other parameters are structure sensitive, which means the properties can be readily altered through tailoring the microstructure.

The Weiss molecular field theory [6] showed that a ferromagnet is divided into regions (domains) within which the magnetization is equal to the saturation value; in different domains the magnetization is in different directions. The magnetization of a ferromagnetic specimen is the sum of the magnetization of these domains. Related to the magnetic domains, the tailoring of magnetic properties can be achieved through manipulation of microstructures according to three length scales:

(a) Single-domain particle size [6]. At very small crystal size, the crystal prefers to remain in a single domain state. The critical size L_c , below which the single-domain crystal will have lower energy, is given for the cubic crystal system by

$$L_c = \frac{1.7\gamma}{\pi^2 M_s^2} \quad (1-1)$$

where γ is the domain wall energy. The reduction of particle size subdivides the material into “single-domain” particles; it will increase the coercivity H_c towards a maximum which is controlled by the magnetic anisotropies. The critical diameter of a particle for iron is of the order of 100 nm [6].

(b) Ferromagnetic exchange length [4, 7-8]. It is the distance over which the perturbation due to the switching of a single spin decays in a soft magnetic material. The ferromagnetic exchange length can be expressed as

$$L_{ex} = \sqrt{\frac{A_{ex}}{\mu_0 M_s^2}} \quad (1-2)$$

where A_{ex} is the exchange stiffness, which is related to the exchange density energy

J_{ex} and can be expressed as $A_{ex} = \frac{J_{ex} S^2}{a^3}$ (S is the Hoffmann ripple parameter, a is the

lattice constant); μ_0 is a constant and equal to $4\pi \times 10^{-7} \text{ H/m}$. This length scale is ~ 3 nm for ferromagnetic iron- or cobalt-based alloys. The concept of ferromagnetic exchange length has motivated the processing of nanocomposite hard magnets. Such magnets are nanoparticles of a magnetically hard phase in a matrix of magnetically soft phase or multi-layers with a soft phase in an oriented hard phase. The mechanism is called “spring exchange hardening”; it yields large storage energy by a combination of high H_c of the hard phase and large M_s of the soft phase.

(c) Domain wall thickness [7-8]. It represents the minimum scale within which the magnetic moments are aligned parallel to one another as a result of exchange interaction. The domain wall thickness is given by

$$L_w = \pi \sqrt{\frac{A_{ex}}{K_1}} \quad (1-3)$$

K_1 is the magnetic anisotropy. When the grain size is larger than domain wall thickness, the grain boundaries act as impediments to domain wall motion, thus fine-grained materials are usually magnetically harder than large grain materials. However, if the grain size D is much smaller than the domain wall thickness, the grain boundary can no longer pin the domain wall motion, and magnetic anisotropy will be averaged over several randomly oriented grains. In such a case, the Herzer model [4] predicts the coercivity H_c has a D^6 dependence. The domain wall widths are about 40 nm and 3.9 nm for Fe and $\text{Nd}_2\text{Fe}_{14}\text{B}$ respectively [9-10].

Other length scales include the coherence radius (R_{coh}), the mean free path for spin electrons, the much longer spin diffusion length for spin-flip scattering and the Fermi wavelength; these can also play a role in altering the magnetic properties [9-10].

Tailoring of magnetic properties can be intrinsic (e.g. chemistry) or extrinsic (e.g., optimization of the microstructure). Optimization of the microstructure is thus very important once the composition is fixed. Optimization of microstructure includes controlling the dimensions and distributions of phases. Through both intrinsic and extrinsic methods, the magnetic properties can be modified to meet property requirements in various applications. Examples are spring magnetic materials, high density magnetic storage media, nanocrystalline soft magnetic alloys.

1.2 Processing of nanomaterials

Nanostructured materials have been processed using a wide variety of techniques. Generally the methods capable of producing very fine grain sized polycrystalline materials can be used to produce nanomaterials. Nanostructured magnetic materials have so far been successfully prepared by melt-spinning [11], ball milling [12], electrodeposition [13-14], ion implantation [15], sol-gel processing [16], reverse micelle method [17-18] etc. Controlled crystallization from the melt-spun amorphous precursor has been found to be effective in processing bulk nanostructured magnetic materials. This has led to three families of soft nanomagnetic materials [19]: Finemet^① (Fe-Si-B-Nb-Cu), Nanoperm^② (Fe-M-B-Cu, M = Zr, Nb, Hf...) and HiTperm^③ ((Fe, Co)-M-B-Cu, M = Nb, Hf or Zr). In these alloys, a typical nanostructure—a high-density of nanoprecipitates (with a size of about 10 nm) embedded in an amorphous matrix has been obtained. Because of exchange effects between a given nanoprecipitate and its neighbors as well as between nanoprecipitates and the amorphous matrix, these nanomagnets have desirable soft magnetic properties. The metalloid elements Si, B, Zr and etc. are important in processing these nanostructures, they stabilize the amorphous phase and decrease the precipitate growth rate [20]; Cu increases the nucleation density by creating heterogeneous nucleation sites through the formation of Cu clusters [19].

^① Finemet is a trade name introduced by Hitachi Metals.

^② Nanoperm is a trade name introduced by Hitachi Metals.

^③ HiTperm is from Carnegie Melon University, USA.

Mechanical milling is also well suited for the production of hard magnetic materials and has been applied to produce heterogeneous systems for permanent magnets and to produce particles for magnetic recording [21]. It has also been used successfully to yield amorphous magnetic powders [22] and nanocrystalline magnetic powders [23-24], thus it is a potentially useful technique to produce soft nanomagnetic materials. The undesirable features of this technique are the strain introduced by milling and contamination of the milling media induced during milling. The strain can be removed by proper annealing; unfortunately the desired microstructures can also be altered during such annealing. However, due to its easy operation, capability of mass production and potential applications in large dimension motors, generators, transformers and other complicated shaped electromagnetic devices, mechanical milling becomes an attractive method for processing nanomagnetic materials [25].

1.3 This project and the objectives

The area of nanostructured magnetic materials has not yet been fully explored and the properties of nanostructured magnets have not been well understood; a few systems have been discovered which exhibit superior magnetic properties and which are successfully being produced for engineering applications. The investigation of nanostructured magnetic materials is thus significant both in science and technology. Co based alloys are relatively less explored although they have advantages such as near zero magnetostriction, good high-frequency permeability, high temperature resistance and good mechanical properties. In this project, two Co based alloys, Co-Si-B-Fe-Ni and Co-Fe-M-B (M=Zr and P), were investigated; two processing techniques were studied and compared: crystallization from melt spun ribbons and mechanical alloying; in both alloy systems, nanostructures were formed.

The objective of this project is to study the crystallization mechanisms of melt spun $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous alloys as well as counterpart studies of mechanically alloyed Co-Si-B based alloys and Co-Fe based magnetic materials.

Commercial available $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ (2714A) and other alloys with similar compositions were reported to have superior magnetic properties, while the mechanism especially the microstructure was unknown. $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ belongs to HiTperm nanostructured soft magnetic system, the Cu deficient in this alloy was considered not to affect the formation of nanostructure, which is in need of clarify. The motivation of this project can be summarized as follows.

(1) Processing of nanostructures and the study of microstructural control of properties are relatively unexplored in Co based melt-spun alloys. The outstanding case of Finemet nanomagnetic alloys shows that superior properties can be obtained by microstructural control. In the case of the Co-Fe based alloys, although it has been found to form nanocrystals easily from amorphous precursors [26], fundamental questions such as the role of Cu in nucleation and growth, the kinetics of nanocrystallization and the thermal stability of the nanocrystals have yet to be resolved. Most of the previous studies focused on composition $\text{Co}_{44}\text{Fe}_{44}\text{Zr}_7\text{B}_4\text{Cu}_1$ which contains copper, however an earlier report had suggested that Cu is not required for nanocrystallization in Co-Fe alloys. The removal of copper will be an advantage since copper is not a magnetic element. Hence a detailed investigation was carried out on melt spun copper free $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy.

(2) Characterization of Co based amorphous alloys, especially crystallization behavior, is the key to processing novel microstructures as well as to study the thermal stability of these alloys. Amorphous magnetic alloys generally have good soft magnetic properties because of the lack of crystalline anisotropies. However, structural relaxation can sometimes cause deterioration of the good soft magnetic properties. Thus investigation of relaxation processes of amorphous alloys is important even in current applications of amorphous magnetic alloys. It has also been reported that the magnetic properties of some Co based amorphous alloys improved after annealing, however detailed investigations were not carried out to study the changes in microstructure

occurring during annealing. Hence in this study, heat treatment of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ was carried out and the changes in microstructure were investigated.

(3) The study of crystallization behavior will result in a deeper understanding of the processes that compete with bulk metallic glass (BMG) formation, thus characterization of the crystallization of amorphous alloys will aid in research of BMG formation in Co and Co-Fe based alloys.

(4) The use of mechanical alloying adds versatility to the composition range that can be processed. Mechanical alloying is a solid-state powder processing technique; the constraints in processing conditions are not as critical as melt spinning. In particular, a wide variety of chemical compositions can be selected for alloying, amorphization and nanostructured materials processing. The alloyed powders can be compacted into complicated shapes and large sizes for various applications in electromagnetic devices. Mechanical alloying of processing Co and Co-Fe based soft magnetic alloys is a developing area of nanomagnetic materials research.

(5) The investigation of the crystallization of melt-spun amorphous alloys can provide information on the diffusivity of the elements, stability of the phases and the relationship between microstructure and magnetic properties. This information can be used to process alloys with similar compositions by mechanical alloying. Comparisons can be made of the microstructures and relaxation process of the materials prepared using the two techniques.

Thus in this project, characterization of the crystallization mechanisms of melt-spun Co based and Co-Fe based amorphous alloys as well as mechanical alloying of these alloys from elemental powders was carried out. The effect of Fe, Ni, P and B on the alloying process, microstructure formation and thermal stability was also investigated.

The flow chart of this research is briefly outlined in Fig. 1-1. Melt-spun ribbons of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ were characterized: first, the relaxation processes

Crystallization of the melt-spun $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy produced an interesting and novel highly modulated nanolamellar structure. Convergent beam electron diffraction (CBED), Kikuchi maps and high resolution TEM (HRTEM) were used to determine the crystallographic characteristics of this nanolamellar structure. In situ hot stage TEM was also used for real time observations of the crystallization process of this melt-spun $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy and the coarsening of this nanolamellar structure.

Specifically, the following topics were investigated.

- (1) Crystallization of a melt spun amorphous cobalt based alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$.
- (2) In-situ crystallization behavior of the melt-spun $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ amorphous alloy.
- (3) Crystallographic characteristics of nanolamellar structure formed by crystallization from the melt-spun $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ amorphous alloy and the coarsening process of this structure.
- (4) Mechanical alloying of Co-Si-B alloys, amorphization and crystallization, as well as the effect of Fe and Ni substitutions on these process.
- (5) Nanocrystallization behavior of a melt-spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy.
- (6) Mechanical alloying of Co-Fe based alloys and the effects of the metalloid elements P and B on the alloying process and microstructural refinement.
- (7) Comparison of microstructure and magnetic properties of the materials processed by melt-spinning and mechanical alloying techniques.

Chapter 2 Literature Review

The development of materials can be attributed to the following aspects: modeling, processing, characterization and property evaluation. Modeling can predict the desirable microstructures, compositions and other factors and higher efficiency during the applications of materials. Processing, meanwhile, makes the model into reality. Characterization and property measurements evaluate the modeling and processing, and help in the exploration of new applications. The development of new magnetic materials is following the same methodology. In this project, new nanostructured cobalt based alloys has been developed. The origin of the idea, i.e., how the magnetic properties can be improved by formation of nanostructures, how to process these materials, and previous work on the relevant alloy systems, will be included in this chapter.

2.1 Magnetism and magnetic materials

2.1.1 Origin of magnetism in materials

The phenomenon of magnetism has been known and exploited for many centuries. From electromagnetic theory and quantum mechanical theory, the magnetic behavior of substances can be understood in terms of the electronic states of the constituent atoms [6, 27-28]. Substances can thus be classified into five categories: diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic and ferrimagnetic materials. However, diamagnetic, paramagnetic and antiferromagnetic materials are so feebly magnetic that they are usually called 'nonmagnetic'. In engineering or commercial parlance, magnetic materials refer to the ferromagnetic and ferrimagnetic materials.

2.1.2 Ferromagnetism and Weiss theory

Ferromagnetism occurs in nine elements: three transition metals (iron, cobalt and nickel, atomic numbers 26, 27, 28 respectively) and six rare earth metals (gadolinium, terbium, dysprosium, holmium, erbium and thulium, with atomic numbers from 64 to 69).

Many alloys consisting of the three transition elements and their alloys with nonmagnetic elements are also ferromagnetic. Many alloys of manganese (atomic number 25) with non-magnetic elements are also ferromagnetic, although manganese is not ferromagnetic.

The theory to explain ferromagnetic behavior was first developed by Weiss [27]. In the Weiss theory, the concept of molecular field (H_m) in ferromagnetic materials was introduced, this field was assumed to be independent of any externally applied field and to be proportional to the magnetization (M).

$$H_m = \omega M \quad (2-1)$$

ω is the Weiss constant. Another important concept introduced is magnetic domains. It was postulated that a ferromagnet is divided into domains within which the magnetization equals to the saturation value. The magnetization in different domains is in different directions, so that the magnetization of a ferromagnet could be small or even zero.

The existence of magnetic domains in materials is related to the exchange energy, demagnetization energy and anisotropy energy [6, 27, 29]. To make the exchange energy minimum, the magnetization should be saturated (one domain); to make the demagnetization energy minimum, the magnet should be subdivided into more and more domains to average out the stray field; the anisotropy arises from the crystalline nature of most magnetic materials, to minimize this quantity, the magnetization should be parallel to the easy magnetization axis. Through the competition of these three energies the magnet remains in a minimum energy state. The magnetic domains in magnetic materials can be larger than the grains or lie within the grains.

The magnetization process of ferromagnets under an applied magnetic field consists of the movement of domain walls and the rotation of magnetic domains towards the applied field. In general, domain wall motion tends to occur in small fields, and magnetization rotation only begins as the field reaches larger values. The ease of domain wall motion and rotation of domains depends on composition, grain size, presence of

impurities and defects, crystal structures, etc; the ease of domain wall motion and rotation is a key factor in determining magnetic properties.

2.1.3 Magnetization in amorphous ferromagnets (metallic glass)

Since long-range order does not exist in metallic glass, the magnetization process of metallic glass is different from that of conventional crystalline ferromagnets. In crystalline ferromagnets, the magnetic properties can be defined by two major factors: the exchange interaction and a weak magnetic anisotropy originating from relativistic interactions [30]. In amorphous ferromagnets, the exchange interaction varies for different pairs of neighboring spins, depending on the distance between them; the preferred spin directions are defined by short-range structural order leading to local random anisotropy. However, amorphous ferromagnetism still leaves many interesting questions unanswered and remains of considerable interest [30-34].

In amorphous ferromagnets, due to the large amount of addition of nonmetals, the net magnetic moment is decreased due to dilution by nonmagnetic elements and modification of the local environment of magnetic carriers [31, 35]. Metallic glass may have either higher or lower saturation magnetization than crystalline alloy with same composition because of atomic short range ordering in metallic glass, charge transfer between metal and metalloid atoms, and spatial distribution of magnetic atoms. The saturation magnetization and Curie temperature of metallic glass are composition dependent [31, 35].

As in the case of crystalline ferromagnets, domains play a role in the magnetization of metallic glasses [36-39]. Although long-range crystalline anisotropies do not exist in amorphous ferromagnets, anisotropies can be induced by local atomic structure and stress. Therefore, actual amorphous ferromagnets are not like the ideal isotropic magnet, in which domain walls do not appear or the spin moments smoothly rotate inside the whole specimen (circular magnetic moment [27]). In amorphous ferromagnets, domains of sharp 180 degree type or the complex maze type are generally observed [40].

2.1.4 Magnetic properties and technical magnetic materials

The magnetic properties often used to characterize a magnetic material include: saturation magnetization M_s , Curie temperature T_c , coercivity H_c , permeability μ and magnetostriction λ , which can be determined from M - H curve or B - H curve (Fig. 2-1).

Fig. 2-1 Magnetic properties of materials as defined from the magnetic hysteresis loop (M - H curve or B - H curve). M_s (B_s)—saturation magnetization (induction), H_c —coercivity, M_r (B_r)—remanence, μ_{in} (χ_{in})—initial permeability (susceptibility), μ_{max} —maximum permeability and W_H —hysteresis loss.

Except for M_s and T_c , most magnetic properties such as coercivity, permeability, hysteresis losses and remanence are very sensitive to the structure, because they are related to the process of domain wall motion and domain rotation during magnetization, which are strongly affected by grain type, shape or size, defects and secondary phases etc., which determine domain shape, size and mobility [5, 6].

For commercial applications, magnetic materials can be classified into three categories: soft magnetic materials, hard magnetic materials and magnetic storage media. The magnetic materials in use today are listed in Table 2-1.

Table 2-1 Commercial magnetic materials, their magnetic properties and applications. [9-10, 41]

Soft magnetic materials	Class	Typical composition	μ_4	H_c (A m ⁻¹)	B_s (T)	Applications
	Ingot iron	99.8%Fe	150	80	2.14	DC applications
	Low-carbon steels	99.5%Fe	200	100	2.14	AC applications
	Silicon iron	Fe-3%Si (oriented)	1400	7	2.01	Power distribution transformers
	Fe-Ni alloys	Fe-5%Mo-80%Ni	80000	0.4	0.78	Electronic transformer and inductors
	Fe-Co alloys	Fe-2%V-49%Co	800	16	2.30	High temperature
	Metallic glass	Fe ₇₈ B ₁₃ Si ₉	-----	2	1.56	Power distribution transformers
	Soft ferrites	MnZn (H5E)	18000	3	0.44	High frequencies
Hard magnetic materials	Class	Typical composition	B_r (T)	H_c (kAm ⁻¹)	$(BH)_{max}$ (kJm ⁻¹)	Applications
	Alnicos	Fe-8%Al-14%Ni-24%Co-3%Cu	1.28	51	44	Loudspeakers and motors
	Hard ferrite	SrFe ₁₂ O ₁₉	0.42	250	42	Loudspeakers and motors
	Rare earth magnets	SmCo ₅	0.87	640	144	Motors
		Nd ₂ Fe ₁₄ B	1.23	880	290	
	Fe-Cr-Co	Fe-10.5%Co-28%Cr	0.98	30	16	Loudspeakers, motors and bias magnet for telephone receivers
	Co-Fe-V	Fe-10%V-52%Co	0.84	19	7	Antitheft labels and thin foil magnets
	Elongated-single-domain magnets	Fe-Co particles	----	90	28	Timing motors, meters, thermostats and relays
Magnetic storage media	Class	Composition	B_r (T)	H_c (kAm ⁻¹)	-----	Applications
	Iron-oxide	γ -Fe ₂ O ₃	0.11	26		Tapes, floppy disks. The first hard disks were coated with an iron-oxide particulate medium. Co- γ -Fe ₂ O ₃ is the most widely used class of particulate recording materials
		Fe ₂ O ₃ -Fe ₃ O ₄	0.15	37		
		Co- γ -Fe ₂ O ₃	0.15	52		
	CrO ₂	CrO ₂	0.15	45		Tapes, thermomagnetic copying
	Iron	Fe	0.30	120		Videotapes, digital audiotapes and videotapes
	Thin film	Co-Cr	----	----		Disks
	Barium ferrite	BaO-6Fe ₂ O ₃	0.12	64		Perpendicular recording media

Co-Fe based alloys have large saturation magnetization and high Curie temperature and have been widely used in electromagnetic devices for high temperature applications. Co-Fe based alloys have also been used in some articles such as antitheft labels, timing motors and relays. Co based alloy thin films have semi-hard magnetic properties and widely used as recording media.

2.1.5 Directions of magnetic materials research

As in the past, the desire for discovery and understanding and the need to optimize practical products is driving magnetism and magnetic materials research. The challenges faced nowadays include a number of aspects, such as the fundamental limitations on

polarization, the superparamagnetic limit and ferromagnetic resonance, which was reviewed by Coey [9-10]. In dealing with the challenges, the following new materials are under consideration [5, 9-10]: nanocrystalline magnetic materials; artificially structured magnetic materials; amorphous magnetic fibers; nanophase magnets based on rare earth transition metal alloys and other new materials with new structures and compositions. New models should be built to explain the magnetism of these new materials, and to predict new structures and compositions.

2.2 Models on improvement of magnetic properties by formation of nanostructures

Many properties of materials are strongly related to microstructures: phases, grain size and phase distribution etc. The size of microstructural features is the key to control of properties. It is well known that when the feature size is comparable with the characteristic length scales, special properties can be expected. As most of the characteristic length scales, such as mean free paths of electrons or phonons, coherency length and screening length, are in nanometer range, change in properties or development of new properties is probable when nanostructures are formed. As the magnetic properties of materials are influenced by magnetic mean free path of spin electrons and magnetic exchange length which are in nanometer range, design and processing of nanostructured magnetic materials has rapidly developed in recent years. Nanocrystalline soft magnetic materials with grain size about 10 nm are expected to have high permeability, large resistivity and comparable magnetization; development of such nanostructured soft magnetic materials is a major focus of current magnetic materials research.

2.2.1 Herzer model: grain size effect

As stated in section 2.1.4, some magnetic properties such as coercivity, permeability and magnetostriction are structure sensitive. In homogeneous magnetic particles, the coercivity is governed by magnetic anisotropies and modified by the effects of defects on

domain formation and domain wall motion; coercivity is considered to have a relationship with the dimension t (assuming a constant pinning defect density) [42]

$$H_c \propto 1/t^n \quad (2-2)$$

n is a constant and is experimentally found to be about 2. Thus in conventional magnetic materials with coarse grain of size D , the coercivity is $(1/D)^2$ dependent. However, below some critical dimension t , it is energetically preferred that each particle is composed of a single domain. For single domain particles without interactions, the relation between coercivity and particle radius r is expressed as (a and b are material constants),

$$H_c \approx a/r^2 - b \quad (2-3)$$

But for single domain particles with interactions, e.g., a high density of nanoparticles embedded in an amorphous magnetic matrix, the result will be different. The Herzer model provides the relation between coercivity and grain size [4, 43]. In the Herzer model, random anisotropy originally developed for amorphous systems was used. As indicated by Herzer, when the grain size is smaller than the exchange correlation length L_w (see section 1.1), the magnetization cannot follow the randomly oriented easy axis of each individual grain; the effective anisotropy is thus an average over several grains. In the random anisotropy model [42], the effective anisotropy $\langle K \rangle$ is

$$\langle K \rangle \approx K_{loc} \left(\frac{l}{L_{ex}} \right)^{3/2} \quad (2-4)$$

Applied to nanocrystalline material, K_{loc} represents the crystalline anisotropy K_1 , and l is the grain size D . Since exchange length is related to $\langle K \rangle$ by $L_{ex} = \sqrt{A/\langle K \rangle}$, in a nanocrystalline material, the effective anisotropy will be

$$\langle K \rangle \approx K_1^4 * D^6 / A^3 \quad (2-5)$$

Because coercivity is limited by the relation $H_c \leq 2\langle K \rangle / M_s$, the coercivity of nanocrystalline should exhibit D^6 dependence, which means that the coercivity can be decreased by formation of nanocrystals. Fig. 2-2 gives the coercivity v/s grain size for

various soft magnetic metallic alloys. Another important magnetic property for soft magnetic material is the initial permeability, which is inversely proportional to $\langle K \rangle$ therefore the initial permeability shows a $1/D^6$ dependence.

Fig. 2-2 Coercivity H_c vs. grain size for various soft magnetic metallic alloys [4]. It shows the D^6 dependence of coercivity for nanocrystalline soft magnetic material and the $1/D^2$ dependence for conventional material with coarse grains.

Ivanov and Lyakhimets [44] have rationalized the Herzer model to calculate the coercivity of amorphous and nanocrystalline magnetic materials at the concept of excitation of domain wall vibrations. In the Herzer model, the assumption is that nanocrystals are exchange coupled. However, the exchange coupling is also sensitive to the local magnetic moment of the interfacial amorphous phase. The Herzer model thus fails to explain thermal dependence of coercivity as well as magnetic hardening observed at the very early stages of crystallization [45]. Hernando et al [45] improved the Herzer model by including the two-phase character of nanocrystalline materials. In their work, exchange coupling between magnetic moments of adjacent crystallites takes place through the amorphous matrix. The exchange stiffness A was substituted by γA , where γ is a parameter varying between 0 and 1 and closely related to the exchange correlation length of the amorphous matrix L_{am} . γ is given in the following form

$$\gamma = e^{-\Lambda/L_{am}} \quad (2-6)$$

where Λ is the average distance between the surface of two adjacent crystals, it is roughly related to the grain size D and the crystalline volume fraction x through

$$\Lambda = D(1-x)^{1/3} - D$$

The macroscopic anisotropy K_I was derived by considering the structural anisotropy and magnetoelastic anisotropy.

$$\begin{cases} K_I = x \frac{\langle K \rangle}{\gamma^3} + \frac{3}{2} \lambda_{eff} \langle \sigma \rangle & (\text{Exchange coupled, } D < D^*) \\ K_I = K_1 x + \frac{3}{2} \lambda_{eff} \langle \sigma \rangle & (\text{Exchange uncoupled, } D > D^*) \end{cases} \quad (2-7)$$

Where $\langle \sigma \rangle$ is the average absolute value of the residual stresses, λ_{eff} is the average magnetostriction constant and D^* is the maximum size of crystallites which are exchange coupled in the two phase system. λ_{eff} and D^* depend on the volume fraction x through

$$\lambda_{eff} = \lambda_c x + \lambda_{am} (1-x) \quad (2-8)$$

$$D^* = L_{ex} \frac{\gamma}{x^{2/3}} \quad (2-9)$$

λ_c and λ_{am} are the magnetostriction for the crystalline and amorphous phase respectively. L_{ex} is the maximum crystalline size sufficient for exchange coupling in single crystalline phase. Based on this model, magnetic hardening during the very early stage of crystallization was considered to be due to domain wall pinning.

The Herzer model has successfully explained the relationship between magnetic properties and microstructures in nanocrystalline Finemet alloys.

2.2.2 Other models on improvement of magnetic properties by nanostructures

(a) “Exchange spring” magnet model. The hard magnetic properties can be also improved by the formation of nanostructures. Kneller and Hawig [5, 42, 46-47] suggested the use of exchange coupling between hard magnetic phase and soft magnetic matrix phase, so that high saturation magnetization can be maintained in hard magnetic phase,

thus both saturation and remanent magnetization can be improved. This model became known as the “exchange spring” magnet model. For a fine grain structure with a mean grain size $d < 20$ nm in $\text{Fe}_{14}\text{Nd}_2\text{B}$ -based magnets, the remanence is considerably enhanced; for two-phase magnets, a small average grain size improves the remanence as well as the coercivity, and the volume fraction of the magnetically soft phase can be increased up to 50% without a significant reduction of the coercive field. This is a significant improvement in magnetic properties.

(b) Layered structure and magnetic storage. Thin film magnetism has developed rapidly in the last two decades, which mainly includes surface anisotropy, interlayer exchange coupling and exchange biasing [48-49]. In thin film magnetic material, the anisotropy depends on the thickness of the film because of the special configurations of atoms in the surface, which may be arranged in a different symmetry compared to atoms in the bulk [50-52]. Sharp interfaces enhance interface anisotropy and lead to perpendicular anisotropy [53-55]. Interlayer exchange coupling occurs when the interlayer is thin enough for the magnetic interaction of neighboring layers [48-49, 56]. This interlayer can be paramagnetic, diamagnetic or antiferromagnetic; usually a layer of metal, such as Cu, Au, Mn or Cr is used. Exchange biasing typically refers to the shift of the hysteresis loop away from the zero axis, recent experiments in thin ferromagnetic and antiferromagnetic films show that large exchange bias field can be obtained, which have been successfully applied in magnetoresistive sensors [42,57]. Thin film magnetic materials have significant applications as data storage media and in magnetic recording heads [49, 58-59].

Besides the Herzer model of the grain size effect on soft magnetic materials, the spring exchange magnet model for hard magnetic materials and models of thin film magnetic materials, there are some other models of nanomagnets, e.g, nanomagnetic particles in a non-magnetic matrix [60-61], nanowires[62], nanomagnetic particles encapsulated by nonmagnetic coatings [5, 17] etc. These models can be important in the development of future nanomagnetic materials. .

2.3 Processing of amorphous and nanostructured magnetic materials

With the development of science and technology, new techniques have been discovered and explored, which provide a variety of opportunities to process new and advanced materials. Greer [63] summarized the techniques to process amorphous metals (Table 2-2). Generally, techniques that process amorphous materials can also be used to process nanostructures. In this section, rapid solidification and solid state reaction techniques to process amorphous and nanostructured materials were reviewed.

Table 2-2 Some processing methods for glassy and amorphous metals [63].

	Method
Rapid liquid cooling	Melt-spinning, planar flow casting Atomization Wire formation in water As a surface treatment Scanned laser or electron beam Pulsed laser beam
Undercooling of clean liquids	Emulsion technique Fluxing Solidification in free fall
Physical vapor deposition	Evaporation Sputtering
Chemical methods	Electroless deposition Electrodeposition Precipitation Hydrogenation
Irradiation	By light or heavy ions By electrons By neutrons Ion implantation Ion mixing
Mechanical methods	Grinding Mechanical alloying
Reactions	Solid-state reaction of elements Decomposition of crystalline solid solution

2.3.1 Melt spinning, rapid quenching

A glass can be produced if a liquid is cooled sufficiently rapidly to avoid crystallization. For conventional oxide glasses, the critical cooling rate is very low; however, for metallic glasses, the cooling rate needed can be very high ($>10^5$ °C/s, some bulk metallic glass can form at lower cooling rates), which cannot be obtained in

conventional solidification techniques. The basic idea to obtain this high cooling rate is to increase the areal thermal conductivity, i.e., use a high thermal conductivity medium and increase the surface area. For example, in melt-spinning and planar flow casting technique, a metal (generally copper) is the cooling medium and a thin ribbon is produced. Melt-spinning has been the main technique for metallic glass production [63].

Only alloys in a limited range of composition have been made into glasses [63-65]. This limitation is related to the glass forming ability of alloys, which is evaluated in terms of the critical cooling rate for glass formation [66-69]. Essentially the glass-forming compositions are those at which the liquid is relatively stable compared to the crystalline phases. Thus deep eutectic compositions are generally selected for metallic glass processing, the solutes which generally stabilize the melt through the entropy effect destabilize the solid solutions through the difficulty of incorporation foreign atoms in the crystal structure [63]. Metallic glasses generally have a composition with atomic size difference more than 10 %. Some alloys are very good glass formers, such as Pd-Si, Mg-Ln-M (Ln=lanthanide metal, M=Ni, Cu or Zn), Zr-Al-TM (TM=VI-VIII group transition metal); they can form bulk metallic glass, with thickness of several millimeters.

Metallic glasses display interesting mechanical properties [70], corrosion resistance [71-72] and soft magnetic properties [73-74] because they lack long range periodic structures and defects such as grain boundaries, dislocations and stacking faults.

The first commercial soft magnetic amorphous alloys in the useful form of continuous ribbons were prepared using melt-spinning technique by Allied Chemical Corporation in 1973 [41]. Generally these alloys consists of ferromagnetic metals Fe, Co and Ni with additions of B, P, C, Si to amorphize the alloys; additional alloying by transition group elements such as V, Nb, Ta, Cr, Mo and Mn are sometimes employed to improve the properties [74]. The typical magnetic properties (Table 2-3) of these classes of amorphous magnetic alloys can be briefly described by the following.

Table 2-3 Magnetic properties of some commercial amorphous magnetic alloys.

Alloy	Composition	B_s (T)	H_c (Am ⁻¹)	λ_s (10 ⁻⁶)	ρ ($\mu\Omega m$)	T_c (°C)	Ref.
Iron-based	Fe ₈₁ B _{13.5} Si _{3.5} C ₂	1.61	3.2	30	1.30	370	[41]
	Fe ₇₈ B ₁₃ Si ₉	1.56	2.4	27	1.30	415	[41]
	Fe ₆₇ Co ₁₈ B ₁₄ Si ₁	1.80	4.0	35	1.30	415	[41]
	Fe ₇₉ B ₁₆ Si ₅	1.58	8.0	27	1.25	405	[41]
	Fe ₇₂ Al ₅ Ga ₂ P ₁₁ C ₆ B ₄	1.07	5.1	2	---	332	[19]
	Fe ₈₀ P ₁₃ C ₇	1.40	5	---	---	314	[73]
	Fe ₈₀ B ₂₀	1.60	3	---	---	374	[73]
	Fe ₈₀ B ₁₁ Si ₉	1.59	2	---	---	392	[73]
	Fe ₈₀ P ₁₆ C ₃ B ₁	1.50	4.0	30	---	---	[75]
	Fe ₇₄ Cu ₁ Nb ₃ Si ₁₃ B ₉	1.25	1.2	0.5	---	535	[75]
Iron-nickel based	Fe ₄₀ Ni ₄₀ P ₁₄ B ₆	0.82	46	11	---	300	[75]
	Fe ₄₀ Ni ₃₈ Mo ₄ B ₁₈	0.88	1.2	12	1.60	353	[41]
	Fe ₄₇ Ni ₂₉ V ₂ Si ₈ B ₁₄	1.0	0.8	70	---	500	[75]
	Fe ₂₉ Ni ₄₉ P ₁₄ B ₆ Si ₂	0.42	56	5	---	---	[75]
Cobalt-based	Co ₆₅ Fe ₄ B ₁₄ Si ₁₅ Ni ₂	0.57	0.3		1.42	225	[76]
	Co ₆₇ Fe ₄ Mo ₂ B ₁₂ Si ₁₂ Ni ₃	0.72	0.4	0.5	1.35	340	[41]
	Co ₇₆ Fe ₂ Mn ₄ B ₁₂ Si ₆	1.10	---	---	---	407	[77]
	Co ₇₂ Fe ₃ P ₁₆ B ₆ Al ₃	0.63	1.2	0	---	350	[75]
	Co ₆₃ Fe ₄ Si ₁₀ B ₁₅ Ni ₈	0.75	0.8	---	---	522	[75]
	Co ₆₃ Fe ₄ Si ₁₀ B ₁₅ Nb ₁ Ni ₇	0.70	0.3	---	---	540	[75]
	Co ₆₃ Fe ₄ Si ₁₀ B ₁₅ Nb ₂ Ni ₆	0.65	0.3	---	---	540	[74]

(a) **Iron-based alloys.** Iron based alloys have relatively high saturation induction, in the range of 1.6-1.8 T. They possess good high-frequency (up to about 100 kHz) characteristics equal to or better than those of crystalline nickel-iron alloys.

(b) **Iron-nickel based alloys.** They have saturation induction around 0.9 T. Their magnetostriction is low compared to the conventional crystalline Fe-Ni alloys and the corrosion resistance is better than the iron-based alloys, but they are more expensive.

(c) **Cobalt based alloys.** These alloys have interesting near-zero magnetostriction properties. These alloys also have good high frequency magnetic properties. They are expensive compared to the other two classes due to their high Co content.

Amorphous magnetic materials have a number of applications in electronic devices, such as power electronics, telecommunication devices, automotive magnetic devices,

positioning sensors, magnetic field sensors, current sensors and electronic article surveillance [73-74, 78]. The advantages of amorphous magnetic materials compared to the conventional crystalline soft magnetic materials include their low magnetic loss, fast flux reversal, high electric resistivity and low acoustic loss. Amorphous magnetic alloys have also been used in medical applications for local hyperthermia and in controlling and monitoring implanted devices [74].

Rapid solidification can also form nanostructures since grain growth can be reduced at low temperature due to the decreased diffusivity. In the conventional solidification process, the grain size is determined by a balance between the nucleation and growth rates; the grain size decreases rapidly, reaches a minimum and then increases rapidly again with increasing undercooling. However, in some alloys, due to solute segregation and trapping during rapid solidification, nanostructures can form [11, 79-80].

Controlled crystallization from an amorphous precursor, for example, melt-spun amorphous ribbon, is the most common and effective method to prepare bulk nanostructured materials. The controlling factors will be reviewed in section 2.4. So far three families of nanocrystalline soft magnetic materials with superior soft magnetic properties have been successfully processed (Table 2-4).

Table 2-4 Three families of nanocrystalline soft magnetic materials. Ref. [19-20].

Alloy name	Typical composition	Nanocrystalline phase	$B_s(T)$	H_c (A/m)	μ ($\times 10^3$)	$\theta_c(^{\circ}C)$
Finemet	$Fe_{73.5}Si_{13.5}B_9Nb_3Cu_1$	α -FeSi, FeSi (DO_3)	1.0-1.2	0.6-3.1	5k-100k	<770
Nanoperm	$Fe_{88}Zr_7B_4Cu$	α -Fe (b.c.c)	1.5-1.8	2.4-4.5	3.5k-48k	770
HiTperm	$Fe_{44}Co_{44}Zr_7B_4Cu$	α -FeCo (b.c.c) α' -FeCo (B2)	1.6-2.1	80-200	1k-5k	>965

The obvious advantages of these nanostructured magnetic materials are the higher magnetic induction and Curie temperatures compared to the amorphous precursors, which indicates a wider range of commercial applications [19]. In particular the recently developed HiTperm alloys have very high Curie temperature and are candidates for high temperature electromagnetic applications. A few other systems and compositions are

being studied to form nanostructures from amorphous precursors and thus improve the magnetic properties.

2.3.2 Mechanical alloying

Mechanical alloying (MA) is a viable solid-state processing route for the synthesis of a variety of equilibrium and non-equilibrium phases [25, 81-82]. MA (generally practiced using the high-energy ball milling technique) is accomplished through mixing, impaction, shearing, cold welding and fracturing. The advantages of mechanical alloying include: (a) extending terminal solid solubility in many commercially important metallic systems, (b) synthesis of high melting point intermetallics with homogeneous structure and

Fig. 2-3 Alloying mechanism of MA. (a) Powders mixing during the collision of two balls. (b) Powders evolution during milling and alloying, typically for ductile-ductile system.

The factors affecting the alloying process include ball-to-powder weight ratio, milling speed, surfactant and other conditions of milling environment such as temperature, gas or vacuum and presence of magnetic field [25, 81-82, 84]. Ball-to-powder weight ratio and milling speed determine the rate of energy that transferred to the powders, alloying therefore can occur in shorter milling time when the weight ratio and speed are higher. Surfactant was generally used to reduce the sticking of powders to the vials and balls. Higher temperature can enhance diffusion, which makes alloying easier [85].

Milling can further refine the microstructures after alloying; it can thus produce non-equilibrium amorphous phases and nanostructures. Solid-state amorphization by MA was first discovered in 1983 [82, 86]. Two possible routes for amorphous formation have been suggested: continuous break-up of particles into smaller crystallites and interlayer diffusion [87-89]. The latter route is more common and observed in some alloy systems. It has been suggested that a large negative heat of mixing of the constituents is required for the easy amorphization using MA. Nanostructures can be formed either directly by continuous refinement of microstructure or by crystallization induced by mechanical

milling of previously formed amorphous structures [90-91]. The exact mechanism of amorphous and nanostructure formation by MA is not well understood.

MA is also suitable for processing amorphous and nanostructured magnetic materials. Magnetic oxide nanocomposites have been successfully processed by MA and have exhibited attractive magnetic properties [12, 92]. Nanocomposite rare earth permanent magnetic materials, which have attracted considerable interest since 1991, have been fruitfully studied by MA [93-94]. MA has thus attracted a large amount of research interest in the last decade [21].

As reviewed in section 2.3.1, amorphous magnetic ribbons prepared by melt spinning have shown superior soft magnetic properties as well as some nanostructured magnetic materials crystallized from melt-spun amorphous precursors. However, the melt-spinning technique has limitations in making large size motors, generators, transformers and complex electromagnetic devices. MA processing of soft magnetic materials is thus motivated by the desire to widen the range of such applications. Many binary systems have been extensively studied for this purpose, such as Fe-Si [83, 95-102], Fe-Co and Fe-Ni alloys [23, 103-108]. However, in these binary alloys, amorphization by MA was found to be difficult. E.g. in Fe-Si alloy system, generally with high Si content ($>25\%$), a partially amorphous can form, metalloid compositions such as P, B, C can ease amorphization and led to higher volume fraction of amorphous phase; in Fe-Co and Fe-Ni systems, only b.c.c or f.c.c crystalline phase can form. Nanocrystal has instead been obtained: in MA Fe-6.0 wt%Si alloy [97], mainly amorphous phase with nanocrystals of about 10 nm were observed by TEM (transmission electron microscopy); in Fe-Co and Fe-Ni alloy systems, the average grain size reached by MA is about 20 nm.

However, large internal strain induced by mechanical milling is a limitation of this technique to produce materials with good soft magnetic properties, despite the formation of amorphous phase or nanocrystalline structure. One pathway to process soft magnetic

materials by MA is to retain the amorphous phase or nanostructure during annealing and at the same time relieve the strain [21]. Stabilization of the microstructure can be achieved by suitable elemental additions. Some examples have been reported: in MA multi-component $\text{Fe}_{80}\text{Zr}_8\text{B}_{11}\text{Cu}_1$ alloy, a nanosized b.c.c soft magnetic phase (about 15 nm) in an amorphous matrix could be obtained after heat treatment [109]; in low energy mechanically milled $\text{Co}_{71.3}\text{Si}_{15}\text{B}_{10}\text{Fe}_{4.7}$ amorphous powders produced from crystalline ribbons, the soft magnetic properties are comparable with metallic glass ribbons and a considerable decrease in magnetocrystalline anisotropy was found in wet milling conditions and by application of surfactant [110].

In order to process soft magnetic materials, the following challenges should be overcome: large stress, contamination and inhomogeneity. To reduce stress, annealing conditions and alloy compositions should be properly selected. Contamination can be introduced by the balls and vial, thus suitable materials to coat the balls and vial should be used; contamination can be also caused by the atmosphere since fine particles are very reactive and will react with the air or gas, selection of milling atmosphere is important [111]. MA Fe-Co powders after annealing at 900 °C for 18 ks in H_2 exhibit nearly the same permeability as that of the ingot produced by conventional casting followed by the same annealing treatment [99]. Bulk MA [25, 112] can be used to reduce the contamination of balls and vial.

Besides rapid solidification and MA, a number of other techniques have been used to process nanostructured magnetic materials. For example, chemical synthesis techniques such as reverse micelle [17], coprecipitation [115], emulsion polymerization [116] and carbon arc methods [117-118] can be used to process magnetic nanoparticles. In order to stabilize nanoparticles, coating with gold or some polymer is necessary. Magnetic nanoparticles can be potentially used in the area of drug delivery, photonic applications, magnetic fluids and high density data storage. Other techniques, such as sputtering [119],

electrodeposition [120], electro-chemical deposition [121] and nanoimprint lithography [122], have been widely used to prepare magnetic thin films, arrays and nanowires. These techniques are powerful in the design of nanostructures and can yield useful nanomagnetic materials.

2.4 Relaxation and crystallization behavior of metallic glasses

Metallic glass, which is generally “quenched” from the liquid state, has a random atomic structure and is metastable. It is well known that the mobility of atoms can increase at elevated temperatures or under an applied field. Metallic glasses thus exhibit property changes relating to the rearrangement of atoms. The process of rearrangement of atoms is defined as relaxation and crystallization of metallic glass.

2.4.1 Relaxation in metallic glass

Relaxation in metallic glass is a minor rearrangement of atoms from “quenched” state. When metallic glass has been annealed below the crystallization temperature (crystallization has not yet occurred), properties such as permeability [123-124], magnetomechanical coupling coefficient [125-126], reluctivity [127], magnetic power loss [128], magnetization [129-130], Curie temperature [131] and activation energy for crystallization [132] change significantly. The change in these properties is generally considered to be due to stress relief and structural relaxation. Although the atomic structure of metallic glass and atomistic details of the structural rearrangement have not been fully understood, structural relaxation can have two components: topological short range ordering (TSRO) and chemical short range ordering (CSRO) [133-135]. Structural relaxation during isothermal annealing of as quenched glass will result in a decrease in the amount of free volume (TSRO) and an increase of the degree of short-range order (CSRO). TSRO and CSRO relaxation are described by the free volume model and activation energy spectrum model respectively [134].

The measurement of relaxation can be carried out indirectly, for example DSC (differential scanning calorimetry) has been used to measure the relaxation enthalpy and determine the relaxation rate [131]. As in crystalline materials, structural relaxation are sensitive to heat treatment and can be determined by measuring the volume change (specifically length change [134]) or elastic modulus [133]. Scott [133] pointed out that the kinetics of initial relaxation of as quenched glass differs from those of sequential reversible ordering and disordering as a consequence of the changes in the excess free volume changes within the glass, which led to faster relaxation of the as quenched metallic glass than that of the pre-annealed samples. Huizer [134] showed that (a) the reversible length effect in amorphous $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ exists; (b) a third effect apart from CSRO and TSRO exists and causes an irreversible length change, (c) the thermal expansion coefficient is independent of structural relaxation.

In practice, preferred soft magnetic properties of amorphous metallic glass can be sometimes obtained by heat treatment above Curie temperature and below crystallization temperature [128, 136]. For heat treatment below Curie temperature, a magnetic field should be applied in the longitudinal axis of the ribbon. These results hint that CSRO relaxation is useful to further improve the soft magnetic properties while TSRO relaxation may not help. Applied magnetic field can increase the mobility of atoms in specified directions and modify the CSRO relaxation process.

The study of relaxation is important because metallic glass often becomes brittle after heat treatment at much lower temperatures than crystallization, which reduces its range of applications.

2.4.2 Crystallization mechanisms

When the mobility of atoms is further increased, e.g. by annealing at high temperature, the energy barrier between the metastable amorphous phase and stable crystalline phase can be overcome and the metallic glass crystallizes. As distinct from relaxation,

crystallization is a long range ordering process; crystallization occurs by nucleation and growth. There are three different modes of crystallization [137-138]:

(a) Polymorphic crystallization. Only one phase is produced and the crystallized phase has the same composition as the glass matrix.

(b) Primary crystallization. Only one crystalline phase is produced, the composition of the crystal phase is different from the matrix. The matrix thus changes composition during the process and subsequently crystallizes by a different mechanism.

(c) Eutectic crystallization, where two phases grow cooperatively with the proportions of the phases that the overall composition of crystallized product is the same as that of the matrix, and the composition of the matrix is unchanged during transformation.

Crystallization of most metallic glass is usually determined by a single mechanism. However, sometimes crystallization occurs by a combination of above mechanisms [137].

The physical properties, such as thermal capacity [139-140], electrical resistivity [141-142], magnetization [143] and elastic modulus [137], change sharply during the crystallization process. These sharp changes of properties can be used to study the crystallization mechanisms indirectly. Among these properties, electrical resistivity measurement and DSC are most frequently used. However, the indirect methods are disadvantaged because a linear relationship between properties variation and crystallization is often assumed, which is not necessarily valid. Direct observation and quantitative measurement through TEM observation can provide a better understanding of the kinetics and the factors controlling the crystallization process [144-145].

The overall crystallization kinetics of metallic glass is generally described using Johnson-Mehl- Avrami (JMA) equation [138-140, 146-147].

$$x(t) = 1 - \exp(-Kt^m) \quad (2-17)$$

where $x(t)$ is the time dependent volume fraction transformed, t is the time, K is a temperature dependent constant and m is the Avrami exponent. K can be expressed as

$$K = K_0 \left(-\frac{\Delta H}{RT} \right) \quad (2-18)$$

ΔH is called “the activation energy of transformation”.

The Avrami exponent m is the sum of two components, i.e. m_n and m_g for nucleation and growth respectively [137]. Typically $m_n=0, 1$ corresponds to quenched in nuclei and steady state nucleation respectively. $m_g=1.5$ is expected for primary growth; $m_g=3$ for eutectic and polymorphic growth. The activation energy of transformation ΔH can be related to nucleation and growth by [147-148].

$$\Delta H = (m_n E_n + m_g E_g) / m \quad (2-19)$$

E_n and E_g are the activation energies for nucleation and growth respectively.

Unambiguous determination of the crystallization mechanism and crystallization kinetics requires careful microstructural observation as well as an independent measurement of nucleation and growth.

2.4.3 Conditions for nanocrystallization from metallic glass

The crystallization behavior of most metallic glasses is complex and crystallization products are variable. The crystallization of metallic glass depends on, e.g., the alloy composition [145, 149-152], heat treatment conditions [149, 152-155], surface treatment conditions [155] and applied force (or stress) [156-157]. The effects of composition on the crystallization products from metallic glasses can be categorized as follows:

(a) Substitutions, which use elements with properties similar to the major element. This type of additional element can change the properties of metallic glass. For example, in Fe based alloys, one can use Co to substitute Fe to change magnetostriction [151], the magnetization and Curie temperature of metallic glasses [149, 158]. In Co based alloys, using Fe and Ni to replace Co can change the Curie temperature and electrical resistivity temperature coefficient [142]. These elements can have significant effects on crystallization behavior such as crystallization temperatures and crystallization products [159-160].

(b) Glass forming elements such as C, Si and B. Such elements can increase the thermal stability of the amorphous phase and change the crystallization mechanisms. Due to their near eutectic compositions, the crystallization mechanism of metallic glass can be changed from eutectic to primary crystallization by deviation from the eutectic composition. E.g., in Co-Si-B alloys, crystallization follows a eutectic mechanism in Co-lean alloys and a primary mechanism for Co -rich alloys [161]. Elements such as C, Si and B can also affect the nucleation mechanism [145] and the morphology of the crystalline products [137].

(c) Size controlling elements such as Cu, Nb, Ta and Zr [149]. These elements are usually alloyed in small concentrations; however they significantly affect the crystallization process and may be responsible for nanocrystallization. Cu is used to increase the number of nucleation sites, which enhance the nucleation density during crystallization. Other elements, due to their poor solubility in the crystals, can slow crystal growth by segregation to the interface of crystal and amorphous matrix.

The composition effects on the crystallization process of metallic glass can be related to thermodynamics, kinetic effects, relevant phase diagrams and the solidification process. The composition of the metallic glass also determines its capability for nanocrystallization.

Heat treatment conditions can modify the crystallization products. Factors controlling the crystallization products obtained from heat treatment include heating rate, annealing temperature, annealing time and cooling process. E.g. in $\text{Nd}_7\text{Fe}_{86}\text{Nb}_1\text{B}_6$ metallic glass, the intermediate phase $\text{Nd}_3\text{Fe}_{62}\text{B}_{14}$ formed at lower heating rates but not at heating rates higher than $60^\circ\text{C}/\text{min}$ [154]. In ternary Co-Si-B and Fe-Si-B alloys, high density nanocrystals were obtained using Joule heating; while a coarse microstructure was generally obtained using conventional heating [149]. It was suggested that heat treatment at high temperature for short time using high heating rates could form nanocrystals.

Cooling rate can also affect the crystallization behavior, e.g., in Fe-Zr-B-Cu metallic glasses, a change in the cooling rate can result in different crystallization products [153].

Due to the special atomic configurations and chemistry at the surface, surface nucleation and growth can occur during heat treatment, which affects the crystallization in the bulk by formation of heterogeneous nucleation site. Surface treatment can affect crystallization process; specifically selected surface treatments, which modify the surface chemistry, can accelerate the crystallization process [155]. Surface crystallization generally leads to a coarse microstructure and should be avoided for nanocrystallization.

Applied force or stress can change the mobility of atoms, altering the crystallization process. Some amorphous materials can crystallize even at low temperatures by high energy mechanical milling [156]. In the Pd-Ag-Si alloy, the crystallization temperatures shifted towards higher temperatures under hydrostatic pressure [157]. However, in Al-Ni-Ce-Fe and Al-La-Ni alloys, the crystallization temperature decreased with increasing pressures [162-163]. The effect of pressure on crystallization was attributed to two factors: densification and atomic mobility; densification can only play a minor role for crystallization, while atomic mobility will be decreased at high pressure and crystallization will be retarded [164]. Zhang [165] observed that the grain size decreased from 28.7 nm to 5.8 nm in a $\text{Sm}_3\text{Fe}_{85}\text{Si}_2\text{C}_5$ amorphous alloy annealed at 650 °C for 5 min when the pressure was increased to 6 GPa.

Nanocrystallization of metallic glasses can thus be realized through composition design and processing. Some excellent opportunities for microstructural control in the crystallization of metallic glasses are suggested by Greer [166].

(a) Primary crystallization behavior. The crystal growth is slow in primary crystallization because of solute partition. This favors microstructural refinement and is significant if the solute diffuses slowly in the glassy matrix around the crystals.

(b) Homogeneous nucleation. Homogeneous nucleation can usually produce a high density of nuclei, grain growth can be thus restricted.

(c) **Inoculation in metallic glass.** In both Finemet and Nanoperm alloys, the addition of Cu, which acts as early stage nucleation site, is very useful in nanocrystallization.

(d) **Spinodal decomposition.** Spinodal decomposition can generate composition variation on a very fine scale.

(e) **Quenched-in nuclei.** Quenched-in nuclei may strongly influence crystallization kinetics, e.g. the crystallization temperature can be decreased if a large density of quenched-in nuclei exists in metallic glass. This density of quenched-in nuclei depends on the thermal history and cooling rate used to prepare the metallic glass.

(f) **Relative rates of nucleation and growth.** If the nucleation is very easy and growth is very difficult, nanocrystallization may be obtained.

2.4.4 Nanocrystallization behavior of Finemet, Nanoperm and HiTperm amorphous alloys

Finemet, Nanoperm and HiTperm are three well known families of nanocrystalline soft magnetic materials. These materials have been successfully prepared by primary crystallization from their corresponding amorphous precursors. Their crystallization behavior has been intensively investigated by a number of researchers. The characteristics of crystallization in these three alloy systems can be helpful for the design of new nanocrystalline materials.

(a) **Finemet alloys (Fe-Si-B-Nb-Cu, trade name: FinemetTM, Hitachi Metals).** Finemet alloys exhibit primary crystallization behavior with crystallization temperature of around 530 °C [20, 167-174]. The significance of the crystallization of this alloy is that: Cu enriched clusters are formed at the temperature range of 350 °C~ 430 °C, which provides heterogeneous nucleation sites and effectively increases the nucleation density of Finemet alloys [149, 170], with 1 at% of Cu, the number of Cu enriched clusters formed is in the order of 10^{24} m^{-3} , which is enough to provide heterogeneous nucleation sites for all the b.c.c./DO₃ Fe-Si crystals; the crystalline size remained almost constant during

crystallization due to rejection of the slower diffusion element Nb to the crystal-amorphous interface and enrichment of the faster diffusion element B in the remaining amorphous matrix. The secondary phase Fe_2B , which is undesirable for soft magnetic properties, formed at heat treatment temperature higher than 620°C [171, 174].

(b) Nanoperm alloys (Fe-M-B-(Cu), M=Zr, Hf or Nb..., trade name: Nanoperm@TM, Hitachi Metals). Nanoperm Fe-Zr-B-Cu alloys crystallized at around 490°C and 600°C respectively for primary and secondary crystallization, with the formation of primary α -Fe and secondary Fe_3Zr phases [175]. Composition was found to affect crystallization behavior and magnetic properties in Nanoperm alloys significantly [175-177]. Higher boron content can lead to more uniform fine microstructure, resulting in better soft magnetic properties. Although Cu is presumed to behave as the early stage crystallization nucleus in Nanoperm alloys [175-176, 178], Cu free Nanoperm alloys exhibited nanocrystallization behavior as well [151]. Crystal growth was not controlled by interfacial migration because no segregation of Zr and B at the α -Fe/amorphous interface was observed [179].

(c) HiTperm alloys ((Fe,Co)-M-B-Cu, M=Zr, Nb, Hf). The HiTperm alloys primarily crystallize into α' -(Co, Fe) at about 510°C with an activation energy of 3.35 eV/atom [180-182]. When the annealing temperature is above 700°C , other crystalline phases (e.g., $(\text{Fe, Co})_3\text{Zr}$ for $\text{Fe}_{44}\text{Co}_{44}\text{Zr}_7\text{B}_4\text{Cu}_1$ alloy) begin to form [19]; these phases are undesirable to obtain good soft magnetic properties.

The crystal formed in HiTPerm alloys can have a size of about 8 nm after annealing at 550°C for 1 h [183]. Unlike the Finemet alloys, the nanocrystals were not randomly oriented and were reported to form clusters in HiTperm alloys. Cu did not have much influence on the microstructure. However, with Cu addition, the onset temperature of crystallization shifted to lower temperatures and the activation energy increased for primary crystallization [184]. The fact that Cu did not increase the nucleation density in

HiTperm alloys was attributed to the substantial Co content of these alloys [18]. Partial substitution of Zr and B by Ta or Mo in $\text{Fe}_{44}\text{Co}_{44}\text{Zr}_7\text{B}_4\text{Cu}_1$ alloy can decrease the activation energy; the ratio of Fe and Co (from 50:50 to 65:35) was found not to affect primary crystallization of HiTperm alloys.

The nanostructures in HiTperm alloys are thermally stable; the grain size can remain in the nanometer range (about 60 nm from Scherrer analysis of XRD results) even for high temperature (600 °C) and long time annealing (3072 h) [26, 180]. Since there was a continuous increase in ordering and coordination of Fe and Co atoms From extended x-ray absorption fine structure (EXAFS) examination of the microstructure in HiTperm alloy [180], it was found that the equilibrium state was not reached even after annealing at 800 °C. EXAFS investigation of the role of Zr in HiTperm alloy indicated that local environment of the Zr atoms remained in the amorphous state. Three dimensional atomic probe (3DAP) elemental maps also showed that the remaining amorphous matrix has higher Zr and Co content [183]. It is possible that the Zr rich remaining amorphous matrix inhibits the growth of primary crystals, however, the good thermal stability of the nanostructures in HiTperm alloys is still not well understood.

The common characteristics of crystallization behavior among these three families are: (a) primary crystallization; (b) a broad exothermal peak in the DSC curve; (c) a large temperature separation of primary and secondary crystallization exothermal peak (more than 150 °C); (d) the microstructure formed during the primary crystallization event consists of nanometer sized b.c.c magnetic crystals (about 10 nm) separated by a high viscosity amorphous matrix.

2.5 Co based and Co-Fe based magnetic materials

Co based and Co-Fe based alloys are two important families of magnetic materials. Co based alloys are able to withstand high temperatures and also possess good corrosion resistance. Co-Fe based alloys, e.g. 49 %Co-49 %Fe-2 %V, have large saturation

magnetic induction and high Curie temperature ($\sim 980^\circ\text{C}$). Co-Fe based magnetic alloys are used in electronics requiring high working temperatures and in air-borne devices where weight savings arising from the high saturation induction are required [41]. Besides conventional Co based and Co-Fe based magnetic alloys, the new comers to these families, such as amorphous magnetic alloys (metallic glass), nanocrystalline magnetic materials, ultrafine magnetic alloy powders also show several property advantages.

2.5.1 Near-zero magnetostriction behavior in Co based metallic glasses.

One of the commercially significant properties of Co based amorphous alloys is their near zero magnetostriction behavior at room temperature, which makes these alloys have the highest permeability as well as reduced sensitivity to stress [77, 185-187]. The near zero magnetostriction behavior occurs in compositions with Co/Fe ratio close to that in zero magnetostriction $\text{Co}_{92}\text{Fe}_8$ crystalline alloy [188], it is considered to be due to short range ordering in amorphous alloys which resembles that of their crystalline counterparts. However, magnetostriction in amorphous alloys has not been well understood. Near zero magnetostriction Co based metallic glasses have been used in sensors and other high frequency electromagnetic devices [189-191].

2.5.2 Characteristics of annealed Co based metallic glasses

The thermal stability of metallic glasses is a subject of considerable interest from the view of both science and technology. Co based metallic glasses have been investigated for this reason as well as to form nanostructures. By the process of relaxation or crystallization of metallic glasses, annealing can dramatically affect the magnetic properties such as permeability, anisotropy field and high frequency characteristics.

(a) **Permeability** [123-124, 185, 192-196]. The very high permeability in cobalt based alloys can be further improved upon proper annealing. Fig. 2-4 shows the permeability variation with annealing in a metallic glass $\text{Co}_{66}\text{Si}_{12}\text{B}_{16}\text{Fe}_4\text{Mo}_2$ (Vitrovac^① 6025),

^① Vitrovac is a trade name of VACUUMSCHMELZE GmbH & Co. KG.

indicating a large improvement of initial permeability after 15 min annealing at 420 °C and 443 °C [192]. In metallic glass $\text{Co}_{66}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_1$ (Metglas®[®] 2714A), improvement in permeability was observed in temperature ranges 150 °C~350 °C and 430 °C~550 °C respectively when annealing for 30 min [123, 194-195]. The improvement in permeability was attributed to the release of local stress and possible nanocrystallization [196].

Fig. 2-4 Initial permeability as a function of time for three annealing temperatures. Ref. [192]

(b) High frequency characteristics. The magnetic properties at high frequencies improved substantially in $\text{Co}_{66}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_1$ (Metglas® 2714A) after annealing (Fig. 2-5). The best magnetic properties were obtained after annealing at 760 K for 30 min; this was suggested to be due to the formation of f.c.c. Co nanocrystals.

Fig. 2-5 (a) Core loss at a frequency of 50 kHz and (b) initial permeability at frequencies of 1 kHz and 50 kHz variation with annealing temperature. Ref. [197].

[®] Metglas is a trade name of Allied-Signal, which was merged with Honeywell with new Company name Honeywell.

(c) **Anisotropy field** [77]. Annealing was found to affect the anisotropy field of some Co based metallic glasses. In Metglas 2714A ($\text{Co}_{66}\text{Fe}_4\text{Ni}_1\text{B}_{14}\text{Si}_{15}$) after annealing at 250 °C, the anisotropy direction changed from longitudinal to transverse. The change of anisotropy field in these Co based alloys is ascribed to a progressive irreversible reorientation of atom pairs towards more stable configurations after annealing.

(d) **Coercivity**. As mentioned in section 2.4.1, annealing above the Curie temperature and below the crystallization temperature can improve the soft magnetic properties in metallic glasses, this was also observed in Metglas[®] 2714A [123]. Fig. 2-6 shows that a significant decrease in H_c occurred at higher annealing temperatures from around 200 °C till 500 °C. The decrease of H_c after annealing at around 500 °C was due to formation of nanocrystals of 2 nm in size [123]. Two step cooling method was suggested to further improve the magnetic properties [193].

Fig 2-6 Coercivity H_c and squareness ratio I_r/I_c as a function of the heat treatment temperature T_{ht} . The isothermal time is 30 min at the heat treatment temperatures. Ref. [123].

(e) **Disaccommodation** [131, 198]. Disaccommodation (DA) refers to the decrease with time of the initial permeability after demagnetization. DA of the metallic glass $\text{Co}_{70}\text{Si}_{10}\text{B}_{15}\text{Fe}_5$ was found to decrease after annealing; it was explained that the annealing treatment decreased the local inhomogeneity [198]. In metallic glass $(\text{CoFe})_{70}(\text{MoSiB})_{30}$,

DA increased at low exciting field but decreased at high exciting field after annealing, due to the anisotropy induced by low field exciting and stress relaxation [131].

(f) Perminvar effect [199-200]. In most Co based metallic glasses with near zero magnetostriction, a similar behavior to perminvar effect was observed on heat treatment between 50 °C and 110 °C below the first crystallization temperature [199]. The origin of the perminvar-like behavior was investigated through Kerr magnetic domain observations to be due to the stabilization of pinned walls in the middle of the sample and nucleation of domain from the sample edge [200].

(g) Giant magnetoimpedence effect (GMI) [126, 201-203]. MI is the effect of the magnetic field on the transverse permeability in the direction of the AC measuring current. Co based alloys with near zero magnetostriction property show GMI effects and have been applied in sensors for magnetic field measurement [201-202].

(h) Microstructure. The crystallization behavior and microstructure have been reported for a few Co based metallic glasses [123, 190, 204-208]. Formation of a microstructure with nanocrystals embedded in amorphous matrix, which is crucial to improve the soft magnetic properties, was reported in metallic glass $\text{Co}_{66}\text{Fe}_4\text{Ni}_1\text{B}_{14}\text{Si}_{15}$ (Metglas 2714A) after isothermal heat treatment at 520 °C for 30 min [123]. Higher temperature (>550 °C) annealing led to the formation of coarse microstructures in this alloy and deteriorated the initial good soft magnetic properties. In $\text{Co}_{95-x}\text{Fe}_5(\text{BSi})_x$ metallic glasses, faulted f.c.c. or h.c.p. Co layers crystallized underneath the borosilicate oxide layer with an approximate thickness relationship of $t_{\text{crystalline Co layer}} = 3.5 t_{\text{surface oxide layer}}$ [190, 206]. The faulted crystalline Co layer was presumed to be induced by oxygen during annealing. When annealed at Ar atmosphere, slightly faulted or unfaulted h.c.p. Co nanocrystals were obtained. Serebryakov [207] reported that textured h.c.p. Co was formed by surface crystallization in the undercooled liquid of $\text{Co}_{72}\text{Fe}_{4.5}\text{Cr}_{1.5}\text{Si}_{12.5}\text{B}_{9.5}$ alloy, followed by decomposition of the underlying amorphous regions into B- and Si-enriched phases; these

phases acted as precursors for formation of f.c.c and h.c.p. Co based phases during annealing. In the primary crystallization of $(\text{Co}_{0.75}\text{Cr}_{0.25})_{80}\text{Si}_5\text{B}_{15}$ metallic glass [208], elongated h.c.p. (Co, Cr) crystals formed after annealing at 500 °C for 30 min (Fig. 2-7 a). Higher annealing temperature led to secondary crystallization of amorphous matrix into σ -CoCr phase (600 °C for 30 min), this phase subsequently decomposed into Co_3B and h.c.p. (Co, Cr) phases. The microstructure was consisted of the mixture of Co and orthorhombic Co_3B phases in crystallized $\text{Co}_{68}\text{Fe}_4\text{Cr}_4\text{Si}_{13}\text{B}_{11}$ alloy (Fig. 2-7 b). The crystallization process was described as the simultaneous precipitation at 500 °C of h.c.p. and f.c.c. Co phases from the amorphous matrix; polymorphous transformation of h.c.p. Co into f.c.c Co accompanied by rejection of B from h.c.p. Co lattice and formation of Co_3B phase.

Fig. 2-7 Microstructure formed in metallic glasses (a) $\text{Co}_{72}\text{Fe}_{4.5}\text{Cr}_{1.5}\text{Si}_{12.5}\text{B}_{9.5}$ [208] and (b) $\text{Co}_{68}\text{Fe}_4\text{Cr}_4\text{Si}_{13}\text{B}_{11}$ [209] after annealing at 500 °C for 30 min.

The development of magnets for high temperature power applications requires new bulk soft magnetic materials that (a) are capable of operating at higher temperatures and (b) possess higher combined inductions and permeabilities [181-182]. HiTperm ($\text{Co}_{44}\text{Fe}_{44}\text{Zr}_7\text{B}_4\text{Cu}_1$) alloys exhibit nanocrystalline structure which is stable even at high temperatures. This nanocrystalline structure was formed after primary crystallization from the melt-spun amorphous precursors, the HiTperm alloys are promising candidates for a number of high temperature soft magnetic applications [182-184].

(a) Nanophase formation. The nanocrystallization behavior of HiTperm alloys was reviewed in section 2.4.4. The nanocrystalline phase formed was ordered α' -(Co, Fe) as determined using synchrotron x-ray diffraction experiments which showed the presence of superlattice reflections [26, 181-182]. From TEM observations and 3DAP (three dimensional atomic probe) analysis, the α' -(Co, Fe) nanocrystals contained about 58 at%Fe, 37 at%Co, 1at%Zr and 3 at%B; the nanocrystals were suggested to form groups with similarly orientated crystals in each group; the remaining amorphous matrix had a higher proportion of Co and Zr (the composition was 34.5 at%Fe, 49.0 at%Co, 10.0 at%Zr, 4.8 at%B and 1.7 at%Cu) [183]. It is known that the α' -(Co, Fe) phase has a high Curie temperature (about 980 °C) and a large induction magnetization. From the Bethe-Slater model, the exchange interaction of the amorphous phase in HiTperm alloys before or after primary crystallization is relatively insensitive to fluctuations in the interatomic spacing compared to the Fe or Ni based alloys, i.e., the exchange interaction will be more effective in HiTperm alloys compared to Finemet and Nanoperm alloys [2].

(b) Magnetic domains. No discernible pinning of domain walls by interfacial boundaries existed in this Co-Fe based alloy through Lorentz microscopy observations, which is consistent with the Herzer model [211]. The domain wall pinned by grain boundaries was observed only in some microcrystalline regions due to surface crystallization.

(c) Magnetization. A significant property of HiTperm alloys is its magnetization behavior at elevated temperatures (Fig. 2-13). The HiTperm amorphous precursor has higher Curie

Fig 2-8 (a) Specific magnetization as a function of temperature in HiTperm amorphous precursors (Ref. [26]). (b) A comparison of HiTperm alloy $\text{Co}_{44}\text{Fe}_{44}\text{Zr}_7\text{B}_4\text{Cu}_1$ with a Nanoperm alloy $\text{Fe}_{88}\text{Zr}_7\text{B}_4\text{Cu}_1$ on the thermal magnetization (Ref. [182]).

temperature (about 600 $^{\circ}\text{C}$) than that of Nanoperm alloy (Fig. 2-8 a) [26] and higher than its crystallization temperature [182], therefore the magnetization remains high during annealing even above the crystallization temperature. The second peak in the magnetization curve of HiTperm alloy (Fig. 2-8 b) was ascribed to the formation of more α' -(Co, Fe) precipitates after secondary crystallization [182]. For extended HiTperm amorphous precursors, in which the Fe, Co ratio is 65:35 or for the cases of partial substitution of Ta and Mo, the magnetization processes are similar [184].

(d) **Hyperfine field** [212]. Mössbauer measurements showed that the hyperfine field increased significantly after annealing, from 29.3 T for as-spun HiTperm alloy to 35 T for crystalline phase and about 30 T for the remaining amorphous phase.

The HiTperm alloys have not yet been well understood. E.g., in order to further improve the soft magnetic properties and explore more useful nanostructured magnetic materials, such questions need to be addressed: (a) does the Cu free HiTperm alloy have a microstructure similar to that of Cu containing alloys? (b) is the Cu free HiTperm as thermally stable as the Cu containing alloy? (c) what is the structure of the nanocrystals which form groups? What are the magnetic properties of the Cu free alloys? Our work on will be carried out to understand these issues.

2.5.4 Mechanical alloying processing of Co based and Co-Fe based magnetic alloys

A potential advantage of MA in processing nanomagnetic materials is that, unlike melt spinning, it is possible to produce nanostructures without using glass forming elements; these glass forming elements are undesirable since they are generally non magnetic. MA and ball milling (BM) have been previously investigated in order to process Co based and Co-Fe based magnetic alloys.

(a) Co based alloys [110, 213-215]. MA/ BM of Co based alloys was aimed at formation of bulk metallic glass (BMG) since only thin dimensional form amorphous alloys was produced by conventional rapid quenching. Through low energy BM, crystallized melt-spun $\text{Co}_{70.3}\text{Si}_{15}\text{B}_{10}\text{Fe}_{4.7}$ ribbons could be completely reamorphized after 50 h milling in argon atmosphere; wet milling in DDAB (didodecyldimethyl-ammoniumbromine) surfactant yielded finer powders which had higher coercivity than powders prepared by dry ball milling; annealing at temperatures lower than 300 °C had negligible effect on magnetic properties while for annealing at 300 °C for 18 h the M_s increased due to stress relaxation [110]. Matyja [213] investigated BM of $\text{Co}_{(78-x)}\text{Fe}_x\text{Si}_9\text{B}_8$ alloys starting from crystallized ribbons as well from crystalline elemental powders: after 100 h milling, nanocrystals formed starting from crystalline elemental powders while amorphous phases formed from Fe-poor crystallized amorphous ribbons ($x < 12$). Nanostructures were also reported in $\text{Co}_{78}\text{B}_{11}\text{Si}_{11}$ alloy using high energy BM and a cyclic amorphous $\leftrightarrow$ crystalline transformation was observed during BM. This mechanically milled $\text{Co}_{78}\text{B}_{11}\text{Si}_{11}$ alloy had

a Curie temperature of around 800 °C and a higher magnetization compared to amorphous or crystallized melt-spun $\text{Co}_{78}\text{B}_{11}\text{Si}_{11}$ ribbons.

Short time milling from amorphous ribbons, e.g. 4 h milling at 200 rpm, yielded amorphous powders, which were successfully hot-pressed into bulk compacts at temperatures slightly lower than the onset of crystallization temperature; the bulk compacts showed a good soft magnetic properties with a low H_c of 23 A/m [215]. It's also found that this short time milling changed crystallization mode from original single stage to a two-stage process due to contamination of milling media and introduction of additional defects which act as preferred sites for nanocrystallization. Formation of bulk nanocomposite by filling nanocrystalline Fe powders into the amorphous Co powders was also attempted [215]. However, the coercivity was large which was suspected to be due to the fact that grain size of Fe powders was larger than the exchange length.

(b) Co-Fe based alloys [23, 103, 105-108, 216-217]. MA of Co-Fe nanocrystalline alloys was attractive in research since Co-Fe alloys have the highest magnetic induction as well as high Curie temperatures, and formation of nanostructures can result in better properties. The $\text{Co}_x\text{Fe}_{1-x}$ alloys produced by MA starting from elemental Co and Fe powders exhibited the same change of saturation magnetization with alloy composition as in thermodynamic equilibrium [23, 103, 105]. Although the grain size reached was around 25 nm, the coercivity was quite high (in the range of 1000~5000 A/m); this was suggested to be due to large internal strains introduced during milling. The MA alloys after heat treatment at 200~400 °C for 5~60 min had a grain size in the range of 20 ~70 nm; they showed a peak coercivity at a grain size of about 28 nm.

Elkalkouli [106] studied the alloying of equiatomic Co-Fe alloy from elemental powders and showed that more homogeneous particles can be obtained for longer milling time and the grain size had an equilibrium value of about 7 nm. The alloyed powders were harder to consolidate than the mixture of Co and Fe powders, due to work hardening and the small grain size in MA powders. Lee [107] compared mechanochemical alloying

(MCA) and MA techniques in processing of nanosized $\text{Co}_{50}\text{Fe}_{50}$ alloy powders and found that the magnetic properties of MA powders were inferior to MCA powders although the grain size of MA powders was about 10 nm and much smaller than that prepared by MCA. It was suggested that MCA powders had smaller internal strain than MA powders and the MCA technique yielded ordered Co-Fe alloy, which contributed to better magnetic properties. Kim [108] adopted two milling methods (cyclic and conventional operation) in order to optimize the milling process and found that smaller grained structure was obtained with less milling time using cyclic milling. The coercivities of Co-Fe alloys powder were large due to the large strain. After annealing at 400 °C and 500 °C, the coercivity decreased considerably and showed a value less than 720 A/m after annealing at 400 °C for 60 min. The significance of Kim's work was that high density (over 95 % of the theoretical density) bulk nanostructured Co-Fe alloy with grain size less than 30 nm was obtained by spark plasma sintering of the powders at 900 °C for 5 min. Milling media affected the alloying of $\text{Co}_{50}\text{Fe}_{50}$ powders. Gonzalez [216] reported that milling with WC vials and balls yielded isolated small particles, milling with steel vials and balls produced particle agglomerates. The mean grain size reached 6 nm after 49 h milling in both media and decreased to 4 nm after 100 h in steel media. Baker [217] reported the effect of the ternary elemental additions C, B, Cu and Zr on the MA nanocrystalline Co-Fe powders. The ternary elements had no significant effect on powder morphology, however, some elemental additions led to a smaller grain size, the coercivity of alloys was in the range of 4000~8000 A/m.

From the investigations described above of MA Co based and Co-Fe based alloys, it is clear that amorphous phases or nanostructures can be obtained by MA. To improve the magnetic properties, microstructural studies, stress relaxation process and thermal stability of the MA metastable amorphous/ nanocrystalline phase must be examined, these aspects have been studied in this work.

Chapter 3 Experimental Techniques and Procedures

The experimental techniques included in this project can be divided into two classes: materials preparation and characterization. Materials preparation includes heat treatment of melt spun amorphous ribbons, mechanical alloying from elemental powders and compound powders, and heat treatment of the mechanical alloyed powders. The starting materials, processing parameters and heat treatment conditions are stated in section 3.1. In this chapter, some characterization techniques are introduced. The equipment used for characterization and the operating parameters are described in section 3.2.

3.1 Materials preparation

3.1.1 Melt-spun amorphous ribbons.

Two types of melt-spun ribbon were included in this project. Their compositions and dimensions are listed in Table 3-1. The samples were kindly supplied by Honeywell Electronics and Prof. D.E. Laughlin of Carnegie Mellon University, USA.

Table 3-1 Descriptions of melt-spun ribbons used in this project.

Composition (at%)	Width	Thickness
Co ₆₅ Si ₁₅ B ₁₄ Fe ₄ Ni ₂	26 mm	20 μm
Co _{44.5} Fe _{44.5} Zr ₇ B ₄	2 mm	50 μm

3.1.2 Mechanical alloying

Mechanical alloying was carried out in a planetary ball miller (Fritsch Pulverisette, model F5) using hardened steel balls and vials. Initially the ball to powder weight ratio was 10:1 for each group of samples listed in Table 3-2. A small sample of powders was retrieved after milling for different periods of time before reaching the longest milling time in the group. For example, in the first group, elemental powders were filled into the vial with the weight ratio of balls to powder 10:1, after milling for 50 min, a small amount of powders was retrieved, the remaining powder underwent further milling; then

after milling for 100 min, powders were again retrieved. Ar was filled into the vials to avoid oxidation during milling. The nominal composition, starting materials and other milling parameters are provided in Table 3-2. The starting materials are Co (99.9+ %, 100 mesh, Aldrich Chemical Company), Fe (99.9+ %, 22 mesh, Alfa Aesar), Si (99%, 325 mesh, Aldrich Chemical Company), B (95-97%, amorphous, Fluka Chemic AG Bucks), FeP (99.5%, Alfa Aesar) and FeB (98%, Alfa Aesar).

Table 3-2 Nominal composition, starting materials and milling parameters.

I. Co based alloys

Group	Composition (at%)	Starting material	Milling speed	Milling time
1	Co ₇₁ Si ₁₅ B ₁₄	Elemental Co, Si and B powders	300rpm	50, 100, 150min
2			300rpm	5, 10, 20h
3			300rpm	1900min, 40h
4			300rpm	80h
5	Co ₆₅ Si ₁₅ B ₁₄ Fe ₄ Ni ₂	Elemental Co, Si, B, Fe and Ni powders	300rpm	50, 100, 150min
6			300rpm	5, 10, 20h
7			300rpm	1900min, 40h
8			300rpm	80h

II. Co-Fe based alloys

Group	Composition (at%)	Starting materials	Milling speed	Milling time
1	Co ₅₀ Fe ₅₀	Elemental Fe and Co powders	300rpm	25, 50, 100, 200min
2			300rpm	5, 10, 15, 20h
3			300rpm	30, 40, 50, 70h
4			300rpm(5h)+200rpm	5, 10, 15h
5	Co _{44.5} Fe _{44.5} P ₇ B ₄	Elemental Fe and Co powders, compound FeP and FeB	300rpm	25, 50, 100, 200min
6			300rpm	5, 10, 15, 20h
7			300rpm	30, 40, 50, 70h
8			300rpm(5h)+200rpm	5, 10, 15h
9	Co _{42.5} Fe _{42.5} P ₇ B ₈		300rpm	25, 50, 100, 200min
10	Co _{41.5} Fe _{41.5} P ₁₄ B ₄		300rpm	25, 50, 100, 200min

3.1.3 Heat treatment

Heat treatment was carried out in a vacuum tube furnace (10^{-5} Torr) with temperature fluctuations less than 2°C . The heating rate, temperature and time of heat treatment were set through a program controlling the furnace. The heating rate was $10^{\circ}\text{C}/\text{min}$ for melt-spun ribbons and $5^{\circ}\text{C}/\text{min}$ for mechanically alloyed powders. Several selected annealing temperatures and times were utilized in this investigation.

3.2 Characterization techniques: principles and experimental details

Differential scanning calorimetry (DSC), four probe electrical resistivity, X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM) were used to characterize the as-prepared and heat treated samples. The principles of these techniques are available in textbooks and will not be included in this section. Here only selected techniques used to get additional information are discussed.

3.2.1 Grain size and strain from XRD data.

For an infinite crystal, Bragg scattering occurs at discrete values of 2θ satisfying the Bragg condition. However, conventional crystalline materials are polycrystalline, i.e., the crystal size is finite, thus the peaks are broadened over a range of angles, as in Fig. 3-1.

Fig. 3-1 Illustration of broadening in XRD peak from a (a) conventional materials and (b) infinite perfect crystal.

Scherrer analysis [19] uses the broadening of peaks and gives a simple method to estimate the grain size. Consider a crystal of thickness D having m planes of inter-planar spacing d , the path difference of x-rays traveling through the full thickness of the crystal at angle θ_1 and θ_2 will be

$$(m+1)\lambda = 2D \sin \theta_1 \quad (3-1)$$

and

$$(m-1)\lambda = 2D \sin \theta_2 \quad (3-2)$$

respectively. By subtraction 3-1 with 3-2, using the approximation $\theta_1 + \theta_2 \sim 2\theta_b$ and $\sin((\theta_1 - \theta_2)/2) \sim (\theta_1 - \theta_2)/2$, the thickness D can be

$$D = \frac{\lambda}{(\theta_1 - \theta_2) \cos \theta_b} = \frac{\lambda}{B_\theta \cos \theta_b} \quad (3-3)$$

B_θ is defined as the breadth of the peak. Due to equipment broadening, a more empirical formula, the Scherrer formula is provided:

$$D = \frac{0.9\lambda}{B_\theta \cos \theta_b} \quad (3-4)$$

Besides grain size, the peak broadening can also be due to lattice strain [25], which is proportional to $\tan \theta$, i.e. the total of the peak broadening can be expressed as

$$B = \frac{0.9\lambda}{D \cos \theta_b} + \eta \tan \theta \quad (3-5)$$

Rearranging equation 3-5:

$$B \cos \theta = \frac{0.9\lambda}{D} + \eta \sin \theta \quad (3-6)$$

η is the strain. Equation 3-6 is the Hall-Williamson equation.

This X-ray method is appropriate to determine grain size in the range of 10~100 nm. A grain size of 50 nm is expected to have about 0.2° broadening.

3.2.2 TEM imaging, crystallography characterization and thickness testing.

TEM uses a high-energy electron beam to transmit electrons through a thin specimen. As different phases and atoms have different levels of interactions the transmitted

electrons, contrast (diffractive or compositional contrast) can arise by the consequent change in direction and energy of the transmitted electrons. The magnification of the transmitted signal is through three sets of magnetic lens (objective lens, intermediate lens and projector lens); focus of the electron beams and magnification of the signals by magnetic lenses is analogous to conventional optics. Conventional operation of the TEM will result in either bright field images (BF), dark field images (DF) or diffraction patterns (DP). Formation of a bright field image or a dark field image is controlled by the objective aperture by selection the passage of the direct beam and the scattered beam respectively. Selective area diffraction aperture is used to limit the area being studied; the area selected by this method is larger than 100 nm for most electron microscopes.

Diffraction patterns are generally used to identify different phases and determine new phases as the DP is directly related to reciprocal crystal structure of the phase. However, solely from selected area diffraction pattern (SADP), it is sometimes difficult to determine the crystallography unambiguously; Kikuchi patterns and convergent beam electron diffraction (CBED) can be used together for this purpose. Kikuchi patterns are formed by incoherently scattered electrons (Fig. 3-2) [218-219]. By observation of Kikuchi patterns, the deviation vector s from exact Bragg condition can be estimated; by systematically tilting the sample, it is possible to obtain two beam conditions and DP from different zone axes. CBED is a versatile microdiffraction technique. The difference between CBED and SADP is that CBED uses convergent beam for illumination and SAD uses parallel (Fig. 3-2 c); CBED provides a pattern of disks of intensity, which can be used to determine the symmetry and space group of a crystal. By a suitable combination of SADP, CBED and Kikuchi patterns, the crystallography of a phase can be determined.

Since CBED requires only a small area, small crystals with a size of about 20 nm can be characterized. This fills in the space of SADP techniques in the characterization of nanocrystalline materials. For smaller crystal size, nanobeam diffraction pattern (NBDP) can be used.

Fig. 3-2 (a) Scattering of electrons when going through the thin specimen. (b) Some of the scattered electrons meet the Bragg conditions; in three dimensions, these electrons (Bragg reflected) form a cone, what we observe is a pair of parallel bright and dark lines where cone is cut by the observation plane. (c) Ray diagram showing CBED pattern formation.

Quantitative analysis, such as precipitate density and volume fraction of the phases, requires the thickness value in the region of interest. To determine the thickness, a number of techniques have been suggested [218]. The contamination spot method is suitable for thickness measurement in most materials, however, it is not available in today's high vacuum TEM. Here the techniques used in this project will be introduced.

(a) **CBED**. As the disks in the CBED contain fringes which increase by one every time the thickness increases by one extinction distance, ξ_g , CBED can be used for thickness determination. This is an accurate method for thickness measurement in crystalline material with coarse grains. In practice, two beam conditions with only one strongly excited hkl reflection are used. In this case, the disks contain parallel fringes (Fig. 3-3 a). Using the definition of deviation s_i for the i th fringe (Fig. 3-3b)

$$s_i = \lambda \frac{\Delta\theta_i}{2\theta_B d^2} \quad (3-7)$$

Fig. 3-3 (a) Two-beam CBED in an Fe foil, showing fringes in the disks. (b) Illustration of thickness measurement using two-beam CBED [218].

Arbitrarily assign $n=1$ to the first fringe, then $n=2$ to the second fringe, etc., use the function

$$\frac{s_i^2}{n_k^2} + \frac{1}{\xi_g^2 n_k^2} = \frac{1}{t^2} \quad (3-8)$$

Then plot $\frac{s_i^2}{n_k^2}$ against $\frac{1}{n_k^2}$, if the result is a straight line from which, thickness t and ξ_g can be determined (Fig. 3-3 b). If the result is not a straight line, assign $n=2$ or $n=3, 4, 5 \dots$ until a straight line is obtained.

Two beam CBED determination of thickness has been used in this project to calibrate the intensity of x-ray energy dispersive spectrum (XEDS).

(b) **XEDS**. The intensity of x-ray peak (corresponding to specific element) varies with thin foil thickness t . [218, 220]

$$I_A = I_A^0 e^{-(\mu/\rho)_{spec}^A \cos(\psi) \rho \frac{t}{2}} \quad (3-9)$$

where I_A is the actual x-ray intensity, I_A^0 is the generated intensity of x-rays of element A,

$(\mu/\rho)_{spec}^A$ is the mass absorption coefficient for the x-ray line of element A by the specimen,

ψ is the take off angle and ρ is the specimen density. $(\mu / \rho)_{spec}^A$ is the sum of the mass absorption coefficients for each element times the weight fraction of that element, i.e.

$$\left(\frac{\mu}{\rho}\right)_{spec}^A = \sum_i \left(\frac{C_i \mu}{\rho}\right)_i^A \quad (3-10)$$

C_i is the weight fraction of element i in the specimen. Values of (μ/ρ) can be found in Ref. [221]. The I_A^0 in equation (3-9) can be calibrated from a foil of a suitable element with known mass thickness ρt .

The thickness can be calculated directly, using equation 3-9, with I_A^0 calibrated using a foil with known mass thickness, $(\mu / \rho)_{spec}^A$ from Ref. [221] and the density of the material. An alternative method is that of using the intensity ratio of K and L line (for elements with $Z > 27$). From equation 3-9,

$$I_{AK} = I_{AK}^0 e^{-(\mu / \rho)_{spec}^{AK} \cos(\psi) \rho \frac{t}{2}} \quad (3-11)$$

$$I_{AL} = I_{AL}^0 e^{-(\mu / \rho)_{spec}^{AL} \cos(\psi) \rho \frac{t}{2}} \quad (3-12)$$

Divide equation 3-11 with 3-12; then use logarithmic form of the equation,

$$\ln \frac{I_{AK}}{I_{AL}} = ((\mu / \rho)_{spec}^{AL} - (\mu / \rho)_{spec}^{AK}) \cos(\psi) \rho \frac{t}{2} + \ln \frac{I_{AK}^0}{I_{AL}^0} \quad (3-13)$$

From equation 3-13, the $\ln \frac{I_{AK}}{I_{AL}}$ is a linear function of thickness in specific material.

However, as density is sensitive to the thin foil thickness, one should be careful when using XEDS method to measure the thickness. This method is not suitable for bent foils and foils with rapid change in thickness; XEDS can be used for materials in amorphous as well as in crystalline form.

(c) **EELS**. EELS is the fastest method for thickness estimation in thin foils. It uses the intensity ratio of zero loss peak and plasmon peak in the spectrum, since the inelastic

scattered electrons increases with specimen thickness. A spectrum with zero loss peak and plasmon peak is shown in Fig. 3-4.

Fig. 3-4 EELS spectrum with zero loss peak and plasmon peaks.

For very thin specimens only single scattering occurs; the thickness can be estimated using the following formula

$$t = \lambda_p \frac{I_p}{I_0} \quad (3-14)$$

In this work, the thickness measured using EELS is slightly smaller than that obtained from the XEDS method; generally the two methods showed good consistency, the difference of thickness between the two techniques is less than 10 %.

3.2.3 Equipment and experimental details.

(a) DSC.

A NETZCH DSC 404C was used. For melt-spun ribbons, dynamic DSC using heating rates of 5 °C/min, 10 °C/min and 20 °C/min as well as isothermal DSC measurement were carried out in a nitrogen gas atmosphere to study the crystallization mechanism. For the mechanically alloyed powders, dynamic DSC at a heating rate of 10 °C/min was used to study the thermal properties and crystallization of selected samples. The operating condition in this case was in vacuum.

(b) XRD.

A SHIMADZU 6000 Lab X-ray Diffractometer with Cu target ($\lambda=1.54056 \text{ \AA}$) has been used for x-ray analysis. The as-spun and heat treated melt-spun ribbons are fixed to a piece of silica glass for x-ray scans. Standard glass holders are used for powder samples prepared by MA. JCPDS data are used to interpret the XRD data

(c) Electrical resistivity measurement.

Fig. 3-5 Schematic set-up for probe electrical resistivity measurements.

Electrical resistivity measurement used a four-probe method. Both dynamic (at elevated temperature) and isothermal (holding at selected temperatures) electrical resistivity measurements were carried out to study the crystallization mechanisms of melt-spun ribbons. The ribbons were cut into a rectangular shape with the length about 35 mm and width about 2 mm for these measurements. The set-up is illustrated in Fig. 3-5. The heating was conducted in a tube furnace. A thermocouple was placed just under the sample for temperature measurement. Dynamic heating was controlled through a software program. Isothermal measurements were controlled manually using temperature readings from the thermocouple under the sample. The temperature fluctuation was less than 2°C during these measurements. Flowing nitrogen gas was used to protect the samples from oxidation.

(d) TEM.

TEM microstructural observations were conducted using a JEOL 200kV TEM. Another modified JEOL 200kV TEM was used for in-situ microstructural evolution studies at elevated temperatures. The ribbon samples used were slightly ground after heat

treatment to remove the grooves (formed during the melt-spinning process) on the surface of the samples; then ion-milled. As-spun samples for conventional TEM observation and in-situ TEM observations were ground to a thin foil of about 10 μ m in thickness and then ion milled. The powder samples were prepared as follows: mix the powders with special epoxy used for TEM sample preparation; fill the mixture into a copper tube; cut the tube into disks about 1 mm in thickness; the disks are then ground, dimpled and ion milled as in conventional TEM sample preparation. XEDS (Oxford) and EELS attachments to the TEM were used to analyze the composition and to measure the thickness of foils.

(e) SEM

A JEOL SEM 5410 operating at 20 kV was used for the morphological observations of MA Co-Fe alloy powders; a JEOL SEM 6360 was used for the MA Co based alloys. XEDS attachments in both instruments were used for compositional mapping. Some of the micrographs were selected to analyze the average powder size and size distribution using AIS software. For each of the analysis, more than 200 powders were included.

(f) VSM

The magnetic properties were tested in LakeShore VSM 6360. Standard sample holders for thin foil and powders were used. During the testing, similar shape and mass of the samples in each type of measurement were used in order to make a good comparison. The saturation magnetization was obtained under a maximum applied magnetic field of 1.0 T. The coercivity for the standard Ni sample is about 2390 A/m.

(g) Software

Software such as CaRIne Crystallography 3.1 and Topas have been used as a combination methods to XRD, TEM (SADP, CBED) to interpret the phases involved in this project.

Chapter 4 Results

This chapter presents the results from the investigations of the crystallization behavior of the Co based alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and corresponding studies of the mechanical alloying of Co-Si-B based alloys, the crystallization behavior of Cu free HiTperm alloy $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ as well as mechanical alloying of the counterpart alloy compositions. DSC, electrical resistivity measurements, XRD, SEM, TEM, in situ TEM and VSM techniques were used in this study. The novel highly modulated nanolamellar structure and its crystallographic characteristics, the compacted dendritic nanocrystals crystallized from HiTperm alloy, and stability of the nanostructures, as well as MA amorphization and nanostructure formation are described in this chapter.

4.1 Crystallization behavior of melt-spun cobalt based amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy and nanostructure formation

The crystallization behavior of the amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy was firstly characterized using DSC and electrical resistivity measurements. The microstructure and phases formed after heat treatment at various conditions was then analyzed using TEM and XRD techniques. Interestingly, a novel highly modulated nanolamellar structure was observed within the grains of the initial crystallization product. A detailed microstructural analysis of the nanolamellar structure using HRTEM, SADP, CBED and Kikuchi maps was then carried out to study the crystallographic characteristics of this nanolamellar structure. Coarsening of the nanolamellar structure was also characterized in detail using TEM microstructural analysis, SADP, CBED and EDX. Real time TEM observations of the crystallization behavior of the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ were made and the coarsening behavior of the nanolamellar structure was studied. A thickness dependent crystallization behavior in this cobalt based alloy was observed and quantitatively characterized.

4.1.1 Physical properties variation with the crystallization event

DSC and electrical resistivity measurements were carried out to study the crystallization behavior of the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ amorphous alloy. Fig. 4-1 shows the DSC results at heating rates of 5 °C/min, 10 °C/min and 20 °C/min respectively. Two sets of exothermic peaks were observed during heating. Consistent with these DSC results, the dynamic electrical resistivity also dropped sharply during the two exothermal transformations (Fig 4-2). Besides the two main resistivity drops, an apparent turning point in the resistivity curve was observed at around 220 °C, corresponding to the Curie temperature of the amorphous alloy, and the resistivity decreased again with temperature from about 700 °C. During the heating, there was around 5 % increase of resistivity when crystallization began. The decrease of resistivity during crystallization events was sensitive to heating rate.

Fig. 4-1 DSC results of amorphous alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$.

Fig. 4-2 Dynamic electrical resistivity variation with temperature. ρ_0 is the resistivity of as-spun amorphous alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ at room temperature.

Table 4-1 Table 4.1 Values from dynamic DSC and resistivity results of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy.

Heating rates		First peak				Second peak
		Peak temperature	Beginning temperature	Ending temperature	Heat transferred	
DSC	5 °C/min	537.5 °C	532.0 °C	545.5 °C	85.6 J/g	636.0 °C
	10 °C/min	543.5 °C	537.5 °C	557.5 °C	86.6 J/g	649.0 °C
	20 °C/min	548.5 °C	544.0 °C	570.5 °C	86.2 J/g	655.0 °C
Resistivity	10 °C/min	-----	530 °C	550 °C	-----	-----
	20 °C/min	-----	530 °C	555 °C	-----	-----

The peak temperatures and heats of reaction are tabulated in Table 4-1, summarizing the results from the DSC and electrical resistivity measurements. The crystallization temperature was found to be 543.5 °C at a heating rate of 10 °C/min.

Isothermal electrical resistivity measurements were conducted at temperatures of 500 °C and 510 °C (Fig. 4-3). The resistivity firstly increased with isothermal time, followed by a decrease to a minimum; it again increased and finally stabilized for both isothermal temperatures. The time required to reach the resistivity maximum is about 2600 s and 800 s at temperatures of 500 °C and 510 °C respectively; the time to reach the minimum is 4800 s and 2000 s respectively.

(a)

(b)

Fig. 4-3 Electrical resistivity variation with time when held at (a) 500 °C and (b) 510 °C of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy. ρ_0 is the resistivity of as-spun amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy at room temperature.

4.1.2 XRD results of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy

The as-spun and heat treated samples were characterized using XRD for phase identification. Fig. 4-4 shows the XRD results of samples heat treated for 4 h at 480 °C, 530 °C and 600 °C. The phases formed after 480 °C and 530 °C heat treatments were difficult to determine using XRD; more detailed phase identification was subsequently carried out by TEM; it was found that the phase was actually a metastable phase (M) which had not yet been reported and which was later shown to have an orthorhombic crystal structure. More details are provided in the TEM results section. For the sample heat treated at 600 °C for 4 h, the phases formed were interpreted to belong to the Co_2B , Co_4B , Co_2Si and h.c.p. Co phases. In order to further investigate the phase evolution process during heat treatment, heat treatments at 420 °C, 460 °C, 480 °C, 500 °C, 530 °C, 560 °C for selected heat treatment durations were carried out. For samples heat treated at 420 °C and 460 °C as well as those heat treated at 480 °C for less than 3 h, only a broad hump corresponding to the amorphous phase was observed (not shown). Fig. 4-5, Fig. 4-6 and Fig. 4-7 are the XRD results of the samples heat treated at 500 °C, 530 °C and 560 °C respectively. Besides the hump corresponding to the amorphous phase, some crystalline peaks were observed for the samples heat treated at 500 °C for 10 min (Fig. 4-5 a and b), which indicated the occurrence of crystallization at this heat treatment conditions, this crystalline phase belonged to the metastable orthorhombic crystalline phase. The sample heat treated for 30 min at 500 °C showed a large amount of crystalline phases (Fig. 4-5 c). The XRD results did not vary significantly for further heat treatments at 500 °C (Fig. 4-5 d and e). At 530 °C, strong crystalline peaks were observed for samples heat treated for 5 min (Fig. 4-6 a); for 30 min and 240 min, the crystalline peaks did not change significantly (Fig. 4-6 b and c); while for heat treatment times of 480 min and 960 min (Fig. 4-6 d and e), the relative intensity of peaks changed significantly, Co_3Si was detected in samples heat treated for 960 min. In the XRD result of the sample heat treated

-----Results: Crystallization of Co based amorphous alloy-----

Fig. 4-4 XRD results of samples heat-treated for 4h at (a) 480°C, (b) 530°C and (c) 600°C in Co₆₅Si₁₅B₁₄Fe₄Ni₂ alloy. The phases formed after 480°C and 530°C heat treatment was found to be a metastable phase (M). The phases formed at 600°C belong to Co₂Si, Co₂B, Co₄B and hcp Co phases.

Fig. 4-5 XRD results of samples heat treated at 500°C. The crystalline peaks belong to a metastable crystalline phase M.

-----Results: Crystallization of Co based amorphous alloy -----

Fig. 4-6 XRD results of samples heat treated at 530 °C. In (a), (b) and (c), the peaks correspond to the metastable phase (M). In (d), the intensity of the peaks changes significantly. In (e), metastable Co₃Si phase is detected.

Fig. 4-7 XRD results of samples heat treated at 560 °C. In (a), the crystalline phase is metastable phase (M). In (b) and (c), metastable Co₃Si are detected. The phases in (d) and (e) are the mixture of Co₂Si, Co₂B, Co₄B and h.c.p. Co, see Fig. 4-4 (c).

at 560 °C for 10 min, crystalline peaks were found to be located at positions identical to those of samples heat treated at lower temperatures (Fig. 4-7 a). The relative intensity of peaks changed rapidly with the heat treatment durations, as shown in Fig. 4-7 (b) and (c). After 240 min and 900 min heat treatment at 560 °C, Co_2B , Co_4B , Co_2Si and hcp Co phases were observed. Because of the fluorescence effect caused by scanning the Co rich alloys using a Cu tube x-ray target, the intensity of the peaks is low. Thus a sample heat treated at 530 °C for 5 min was scanned using Cr tube in a PANalytical high resolution X-ray diffractometer. The result is shown in Fig. 4-8, together with a simulated XRD result based on the TEM crystallography analysis. The lattice parameters of the metastable crystalline phase (M) initially crystallized from the amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy are then refined to be $a=0.74118$ nm, $b=1.06735$ nm and $c=0.76800$ nm.

Fig. 4-8 XRD result of a sample heat treated at 530 °C for 5 min, together with the simulated XRD peaks. Experiment was carried out in a Philip Lab X-ray using Cr tube ($\lambda=0.22909$ nm). The simulated XRD peaks are from an orthorhombic crystal with $a=0.74118$ nm, $b=1.06735$ nm and $c=0.76800$ nm and space group of *Cmmm*.

4.1.3 Overall microstructural evolution of the Co₆₅Si₁₅B₁₄Fe₄Ni₂ alloy

TEM was used to study the microstructural evolution in the Co₆₅Si₁₅B₁₄Fe₄Ni₂ amorphous alloy for different heat treatment conditions. Fig. 4-9 shows microstructures of samples heat treated at 500 °C for 10 min, 30 min, 80 min and 160 min. In the sample

4-9 a); the shape of the crystals can be flower-like, hexagonal or twinned, as shown in Fig. 4-10. The samples heat treated for 30 min at 500 °C showed only large crystals, no amorphous phase was detected (Fig. 4-9 b). Some fine precipitates were observed at the grain boundaries of samples heat treated at 500 °C for 60 min (Fig. 4-9 c). After 160 min heat treatment, a large volume fraction of fine precipitates was observed at the grain boundaries as well as inside the grains (Fig. 4-9 d).

Fig. 4-9 Microstructures of samples heat treated at 500 °C. Arrows refer to the fine precipitates.

Fig. 4-10 Three type of morphology of the first stage of precipitation. The sample was heat treated at 500 °C for 10 min.

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Fig. 4-11 Microstructures observed in samples heat treated at 530 °C. The black arrows in (b) refer to the regions of fine precipitates; the white arrows in (c), (d) and (e) refer to the heterogeneous microstructure.

(a) 10 min

(b) 60 min

(c) 240 min

(b) 900 min

Fig. 4-12 Microstructures of samples heat treated at 560 °C. The black arrows in (a) refer to the fine precipitates at grain boundaries and within the grains; the white arrows in (b) refer to the heterogeneous microstructure.

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(a) 60 min

(b) 1440 min

Fig. 4-13 Microstructures of samples heat treated at 600 °C. Arrows refer to the faulted crystals.

Fig. 4-14 (a) Microstructure of a sample heat treated at 700 °C for 240 min. (b) Some of the crystals were etched away during the sample preparation

Table 4-2 EDX compositions analysis of crystals indicated in Fig. 4-14. Group 1:Co rich (~ 90%) and Si lean (~3 %), Group 2: Co lean (~60 %) and Si rich (~30 %), and Group 3: Co rich (~85 %) and Si rich (10 %).

No.	Group			Co (at%)	Si (at%)	Fe (at%)	Ni (at%)
	1	2	3				
1	—			90.2	3.1	6.0	0.7
2		—		63.3	33.5	1.0	2.2
3		—		58.4	38.2	1.2	2.2
4		—		63.1	33.7	1.3	1.9
5		—		57.8	38.4	1.0	2.8
6	—			92.4	6.1	0.5	1.0
7		—		59.3	38.2	0.6	1.9
8		—		60.9	36.1	0.9	2.1
9	—			86.4	4.3	9.3	0.0
10	—			91.5	2.6	2.5	3.4
11	—			87.2	4.4	8.4	0.0
12		—		64.2	29.3	5.0	1.5
13		—		70.8	29.2	0.0	0.0
14		—		59.8	33.1	2.6	4.5
15			—	83.5	10.6	5.9	0.0

Fig. 4-15 SEM micrograph of a sample dynamically heated to 900 °C and cooled. The sample was etched using a dilute chromium acid.

4.1.4 Nanolamellar structure and crystallographic characteristics

A very interesting nanolamellar microstructure was observed inside the large crystals formed after various heat treatments (Fig. 4-16). The nanolamellar structure has a wavelength of about 10 nm and is very periodic. It was observed within large crystals crystallized from the amorphous matrix in the sample heat treated at 500 °C for 10 min; a large amount of amorphous phase remained in this sample (Fig. 4-16 a). In the flower like crystal clusters, the nanolamellar structure in neighboring crystals shows a twinning relationship; the centre of the crystal cluster did not consist of a nanolamellar structure. Inside all the large crystals the same nanolamellar structure can be observed; usually some fine precipitates were observed at the grain boundaries (Fig. 4-16 b). The good periodicity was retained even during subsequent transformation when a large volume fraction of heterogeneous microstructure was also observed (Fig. 4-16 c). Fig. 4-17 shows the HRTEM micrographs and their corresponding SADPs. From the HRTEM, it can be seen that the lattices match well in the neighboring lamellae. SADP of nanolamellar structure showed extra spots perpendicular to the plane of the nanolamellae.

The unit cell in the HRTEM was rectangular and each wavelength of the nanolamellae contained 8~9 layers of unit cells.

The crystallographic characteristics of the crystals that containing the nanolamellar structure was characterized by Kikuchi map observations, SADP and CBED. Fig. 4-18 (a) shows the schematic Kikuchi map; the corresponding SADPs at major zone axis are shown in Fig. 4-18 (b). The crystal was found to have a C base centered orthorhombic crystal structure with $a = 0.74$ nm, $b = 1.07$ nm and $c = 0.77$ nm. (A simulated XRD result using these crystal parameters is shown in Fig. 4-8, showing good match to the experimental XRD results). The planes (2 0 0), (0 2 0) and (0 0 1) are mirror planes. Extra spots was observed in the SADPs numbered 3, 4 and 5 (Fig. 4-18), these spots are located symmetrically from the main reflections and parallel to the (0 0 1) reflection vector. In the SADPs numbered 9 and 10 (Fig. 4-18), asymmetrically located extra spots were also observed; they were perpendicular to the lamellar in the corresponding bright field image. Fig. 4-19 are the CBED from different zones together with the corresponding SADP, it can be seen from the micrographs that: both $[1\ 0\ 0]$ and $[0\ 0\ 1]$ zones have a $2mm$ symmetry in bright field (BF) and in the whole pattern (WP) (Fig. 19 a&b); both $[1\ 1\ 0]$ and $[0\ 1\ 1]$ zones exhibited $2mm$ symmetry in BF and m symmetry in the WP (Fig. 19 c&d); the $[1\ 1\ 2]$ zone shows a 1 symmetry in WP and a 2 symmetry in BF (Fig. 4-19 e). Fig. 4-19 (f) shows the CBED from $[0\ 1\ 0]$ zone in a thin area: extra disks can be observed.

EELS mapping of the nanolamellar structure shows the periodical distribution of boron concentration relating to the nanolamellar structure (Fig. 4-20).

(a) Nanolamellar structure in the precipitates from the amorphous matrix (HT: 500 °C, 10 min).

(b) Nanolamellar structure in fully crystallized samples (HT: 500 °C, 80 min, left; 530 °C, 60 min, right.)

(c) Nanolamellar structure at a stage in which a large portion of the structure has been consumed by the subsequent phase transformation (HT: 530 °C, 240 min, left; 530 °C, 960 min, right).

Fig. 4-16 Nanolamellar structure at different stages of transformation.

Fig. 4-17 (a) and (b) HRTEM micrographs of nanolamellar structure and (c) the corresponding SADP, Z.A.= [1 1 0].

(a)

(b)

Fig. 4-18 (a) Schematic Kikuchi map and (b) the corresponding SADPs.

(a)

(b)

(c)

Fig. 4-19 CBED from zone (a) [100], (b) [001], (c) [110], (d) [011], (e) [112] and (f) [010]. From (a), (b), (c) and (d), the point group was determined to be mmm . (a) and (f) showed the extra disks in (001) diffraction.

Fig. 4-19 CBED from zone (a) [100], (b) [001], (c) [110], (d) [011], (e) [112] and (f) [010]. From (a), (b), (c) and (d), the point group was determined to be mmm . (a) and (f) showed the extra disks in (001) diffraction. (Continued)

Fig. 4-20 EELS boron map of the nanolamellar structure.

4.1.5 Coarsening of the nanolamellar structure

This nanolamellar structure was consumed by the subsequent transformation— which is that of coarsening. Fig. 4-21 shows the precipitates at the grain boundaries, the shape of the precipitates varies with the orientation relationship between the nanolamellae in the neighboring grains as well as with the orientation relationship between grain boundary and nanolamellae. Table 4-3 lists the compositions of both the grains with the nanolamellar structure and the precipitates. The precipitates are Si-rich compared to the grains with the nanolamellar structure. Some of them have a composition close to Co_2Si (bold font, No. 3, 5, 10, 11 and 13); such phases have a lower Fe content; the others are Co rich and Si rich phases; the precipitates with these two featured compositions are spaced alternatively in Fig. 4-21 (b). These precipitates at the grain boundaries later developed into a coarse lamellar structure (Fig. 4-22).

Some precipitates are also observed from within the grains with the nanolamellar structure (Fig. 4-23). These precipitates have a rod shape, lying along the faces of the nanolamellae. The rod shaped precipitates have a relatively larger size when they lie

along a crack (Fig. 4-23 a). When there is no such defect, the width of the precipitates equals to the width of two nanolamellae (Fig. 4-23 b c & d). Fig. 4-24 shows a typical microstructure in the centre of the heterogeneous microstructure and the corresponding SADP, the sample was heat treated at 530 °C for 480 min. The SADP consisted of two sets of DPs: one is tetragonal Co_2B (Z.A.= [1 -1 1]) and the other can be indexed as either orthorhombic Co_2Si (Z.A.= [0 0 1] or hexagonal Co_3Si (Z.A.= [0 1 0]).

(a) 530 °C for 30 min

(c) 530 °C for 480 min

(b) 530 °C for 30 min

(d) 530 °C for 480 min

Fig. 4-21 Precipitates at the grain boundaries. The precipitates shape depends on the orientation relationship between nanolamellae in the neighboring grains as well as the relationship between grain boundary and nanolamellae. In (a) and (b), the nanolamellae are parallel in the two neighboring grains; in (c) they have an acute angle; and in (d) they are near perpendicular.

Table 4-3 EDX determination of the composition of grains with the nanolamellar structure and grain boundary precipitates in Fig. 4-21 (c) and (d).

No.	Co (at%)	Si (at%)	Fe (at%)
1	78.6	15.3	6.1
2	77.4	17.3	5.3
3	68.5	29.2	2.3
4	74.0	22.7	3.3
5	68.0	31.4	0.6
6	73.9	23.1	3.0
7	66.4	31.8	1.8
8	76.9	17.1	6.0
9	77.1	17.1	5.8
10	65.8	32.6	1.6
11	65.4	32.0	2.5
12	67.0	30.9	2.1
13	68.3	29.7	2.0

(a) 530 °C for 60 min

(b) 530 °C for 480 min

Fig. 4-22 Coarsened nanolamellar structure from grain boundaries.

also analyzed using SADP to analyze the matrix phase (Fig. 4-26), which was then found to belong to the hexagonal Co_3Si phase. SADP in Fig. 4-26 (c) corresponds to the $[0\ 0\ 1]$ zone axis.

(a)

(b)

(c)

(d)

Fig. 4-24 (a) Inner heterogeneous structure and (b) the corresponding SADP. The SADP was interpreted to be from Co_2B and Co_2Si phases (indexed using italic font) or Co_3Si (indexed using bold font). The sample was heat treated at 530 °C for 480 min.

EDX composition analysis was carried out to determine the phases in conjunction with the SADP results. Fig. 4-27 (a) shows a part of the heterogeneous microstructure. The faulted phase, which was slightly Co and Fe rich (Table 4-4), was found from CBED analysis to belong to the f.c.c Co phase (Fig. 4-27 b). The white precipitates numbered 3, 6, 9, 10 and 11 were Si rich; the atomic ratio Co/Si was very close to the Co_2Si . Composition numbered 12 is from a large region of Fig. 4-27 (a).

In section 4.1.4, it was shown that the heterogeneous microstructure evolved to equiaxed grains. The composition analysis (Table 4-5) of these equiaxed grains (Fig. 4-28 a) shows a network distribution of three type of compositions: Co rich (~ 90 at%) and Si lean (~ 1 at %); Co (~ 60 at%) and Fe lean (~ 1 at%), Si rich (>30 at%); an intermediate composition of Co (~ 80 at%) and Si ($\sim 10\%$). The grains number 9 and 19 were determined from SADP to belong to the Co_2Si phase and f.c.c Co phase respectively (Fig. 4-28 b & c). Grain 19 is a highly stacking faulted (multiple twinned) grain, the SADP showed obvious elongated spots\lines.

Fig. 4-25 (a) Heterogeneous microstructure; (b) is the magnified part of (a) and (c) is after tilting about 4° from (a). (d), (e) and (f) are the DPs from the area circled in (a), (b) and (c) respectively. (e) f.c.c Co of zone $[1\ 0\ 1]$; (f) orthorhombic Co_2Si of zone $[0\ 0\ 1]$ or from hexagonal Co_3Si of zone $[0\ 1\ 0]$, as indexed in Fig. 4-24 (b). The sample was heat treated at 530°C for 480 min.

Fig. 4-26 (a) Heterogeneous microstructure; (b) was after tilting about 8° from (a); (c) and (d) are SADPs from the circled area in (b). The SADP correspond to the hexagonal Co_3Si phase. (c) Zone axis [0 0 1]; (d) zone axis [0 2 1]. The sample was heat treated at 530 °C for 480 min.

4.1.6 Magnetic properties of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy

The soft magnetic properties deteriorated after crystallization. Fig. 4-29 shows the hysteresis loops of the melt spun sample as well as samples heat treated at 500 °C for 10 min, 530 °C for 5 min, 530 °C for 480 min and 530 °C for 960 min respectively. It can be seen that the coercivity increased monotonically with these heat treatment durations. The hysteresis loop of the sample heat treated at 500 °C for 10 min has a large initial permeability, which is comparable with that of as received samples. The saturation magnetization and coercivity determined from VSM measurement are listed in Table 4-6.

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For samples heat treated at 480 °C, the coercivity and the magnetization did not vary significantly for heat treatment time less than 180 min; the coercivity H_c increased to 7140 A/m and magnetization M_s decreased to 0.469 T for the sample heat treated for 240 min. For heat treatment at 530 °C and 560 °C, H_c increased with heat treatment time; M_s

Fig. 4-27 (a) Heterogeneous microstructure. (b) CBED of the faulted phase in (a); it was indexed to be f.c.c Co, Z.A.=[0 0 1].

Table 4-4 Compositions of the phases in Fig. 4-27 (a).

No.	Co (at%)	Si (at%)	Fe (at%)
1	81.8	12.3	5.9
2	82.3	14.3	3.4
3	69.0	29.4	1.6
4	81.0	15.8	3.2
5	73.2	24.1	2.7
6	67.7	30.7	1.6
7	65.7	33.8	0.5
8	62.40	36.45	1.15
9	63.3	36.3	0.4
10	71.5	26.3	2.2
11	61.3	38.1	0.6
12	80.0	17.5	2.5

(a)

(b)

(c)

Fig. 4-28 (a) Network distribution of composition of equiaxed grains. (b) SADP of grain numbered 9 in (a), it was orthorhombic Co_2Si phase of zone $[1\ 0\ 1]$. (c) SADP of faulted grain numbered 19 in (a); it was multi-twinned f.c.c Co phase of zone $[1\ 0\ 1]$, the mirror plane was $(1\ 1\ 1)$ plane. The sample was annealed at 700 °C for 240 min.

Table. 4-5 Compositions of equiaxed grains numbered in Fig. 4-28 (a).

No.	Co (at%)	Si (at%)	Fe (at%)	Ni (at%)
1	92.2	0.3	5.8	1.6
2	92.2	0.9	6.4	0.5
3	90.7	1.7	7.4	0.2
4	62.1	34.6	1.2	2.1
5	61.0	36.1	0.8	2.1
6	64.0	32.4	0.9	2.7
7	61.8	35.3	0.7	2.2
8	63.0	33.5	0.9	2.6
9	65.4	31.8	0.9	1.9
10	62.4	34.4	0.7	2.5
11	60.1	37.8	0.4	1.7
12	62.4	34.6	1.3	1.7
13	61.8	35.2	1.1	1.9
14	62.3	34.8	0.7	2.2
15	83.6	6.1	9.0	1.3
16	82.4	9.9	6.8	0.9
17	80.6	11.0	6.9	1.5
18	82.5	8.7	7.8	1.0
29	81.3	10.5	7.1	1.1
20	82.7	10.0	6.6	0.7
21	81.9	10.1	6.6	1.4
22	83.2	8.7	7.0	1.1

Fig. 4-29 Magnetic hysteresis loop of as spun and heat treated amorphous alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$.

was approximately 0.5 T. For heat treatment at 600 °C, H_c decreased with heat treatment time and M_s increased with heat treatment time, it appears that the largest H_c corresponds to the smallest M_s .

Table 4-6 Magnetic properties of as-spun and heat treated amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy.

Heat Treatment Conditions		Coercivity (A/m)	Magnetization (T)
Temperature (°C)	Time (min)		
As-spun		80	0.588
480	5	120	0.578
	60	40	0.562
	120	250	0.557
	180	20	0.615
	240	7140	0.469
500	10	890	0.479
530	5	11170	0.441
	30	14120	0.476
	60	15180	0.478
	240	13810	0.514
	480	19000	0.465
	960	23280	0.444
560	10	10800	0.484
	60	19690	0.496
	120	16040	0.520
	240	23390	0.492
	900	22680	0.445
600	60	26550	0.456
	240	23240	0.482
	1440	8390	0.488

4.1.7 In situ crystallization behavior of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ amorphous alloy.

In order to obtain a deeper understanding of the crystallization kinetics of the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ amorphous alloy, in situ hot stage TEM was carried out. The crystallization event in the thin foil occurred at around 400 °C during dynamic heating. The thin foil sample was held at this temperature and in-situ real time TEM observations

of the isothermal crystallization process were carried out. Fig. 4-30 shows the selected micrographs from in situ observations. After 150 s, a high-density of nanocrystals with a size of about 10 nm were observed in the thin regions (Fig. 4-30 a). The density of the crystals decreased with increasing thickness; the size of the crystals increased with increasing thickness (Fig. 4-30 b&c). With increased holding time, the density and size of crystals increased: in the thin regions, the size of the crystals reached about 15 nm after holding for 5900 s (Fig. 4-30 d); in the thick regions, the density of the crystals increased significantly and the size varied in the range of 20 nm to 60 nm (Fig. 4-30 e). Fig. 4-30 (f) is from the same region as Fig. 4-30 (e) and for longer holding time, demonstrating that the crystals changed in shape and size as holding time increased although this changing of shape and size was insignificant.

The thickness dependence of crystallization products is shown in Fig. 4-31. This sample was observed in conventional TEM after the in situ work was completed, i.e., after holding at 400 °C for about 8000 s. From the thin edge to the interior of the sample (the edge refers to the thinnest region which is closest to hole of thin foil TEM sample, the interior refers to the thicker regions neighboring to the hole), the morphology of crystals was clearly seen to vary from a regular shape to a highly faulted irregular shape; the size varied from about 20 nm to more than 100 nm. Quantitative measurement of the average crystal size and nucleation density is provided in Fig. 4-32, the method is provided in Chapter 3 *Experimental techniques and procedures*. The crystals increased in size from about 20 nm to 185 nm as the thickness increased from 80 nm to 320 nm. The nucleation density decreased sharply with increasing thickness from 80 nm to 150 nm; the nucleation density was nearly zero for the thicknesses larger than 300 nm.

Fig. 4-30 In-situ TEM micrographs. (a), (b) and (c) are from the thin regions, the regions with medium thickness and the thick regions. (d) is from the thin regions after holding for a long time of 5900 s. (e) and (f) are from the same region with medium thickness and held at 400°C for 6800 s and 7050 s respectively.

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Fig. 4-31 Thickness dependence of the size and density of precipitates.

Fig. 4-32 Thickness dependence of the precipitate size and the nucleation density.

The crystal structure of the crystallization products in both thin and thick regions was determined using SADP and CBED (Fig. 4-33). In the thin regions, the ring pattern was found to belong to h.c.p Co (Fig. 4-33 a&b). The DP of the thin regions after cooling down contains some spots which do not correspond to h.c.p phase; these extra spots may belong to the f.c.c. Co phase. The DP from the region with medium thickness (Fig. 4-33 c) corresponds to a h.c.p phase of zone axis $[1\ 2\ 2]$; the DP of the $[1\ 2\ 2]$ zone axis of h.c.p. Co phase is close to that of zone $[1\ 1\ 2]$ from f.c.c Co. f.c.c Co phase was observed in the thick regions (Fig. 4-33 d). The crystallization product in the thick regions is a cluster of crystals of twinned h.c.p Co phase and f.c.c Co phase (Fig. 4-33 e).

Fig. 4-33 Crystallization products from (a) thin area (in-situ SADP), (b) thin area after cooling; (c) area with medium thickness, (d) thick area. (e) A precipitate from the thick area was analyzed at various tilting angles. CBEDs (right) in (b), (c), (d) and (e) are from the circled area in the micrograph (left).

(e)

Fig. 4-33 Crystallization products from (a) thin area (in-situ SADP), (b) thin area after cooling; (c) area with medium thickness, (d) thick area. (e) A precipitate from the thick area was analyzed at various tilting angles. CBEDs (right) in (b), (c), (d) and (e) are from the circled area in the micrograph (left). (Continued)

4.1.8 In situ TEM observation of coarsening process of nanolamellar structure.

In-situ TEM was also carried out for a real time observation of the coarsening process of nanolamellar structure. The crystallized sample (dominated by the nanolamellar morphology) was heated to about 500 °C and held at this temperature to study coarsening behavior. The phase transformation was rapid at the heat treatment temperature of 500 °C. Fig. 4-34 provides an overview of microstructural evolution process. From the initial highly modulated nanolamellar structure (Fig. 4-34 a), a high density of spherical precipitates were formed after annealing for 400 s (Fig. 4-34 b), the bulk of the nanolamellar structure has undergone no change at this stage; at a later stage, the nanolamellar structure showed a corrugated appearance, contrast change in some parts of the grain were observed (Fig. 4-34 c); finally, the nanolamellar structure disappeared and was transformed to a multiphase structure (Fig. 4-34 d).

The detailed evolution process in each step is shown in Fig. 4-35, Fig. 4-36 and Fig. 4-37 respectively. The density of the spherical precipitates which appeared after just a few seconds of annealing at 500 °C increased slightly after holding for longer time (Fig. 4-35 a and b). A few precipitates grew larger while most of them did not change much in size during annealing up to 5300 s (Fig. 4-35 c and d); at the same time, larger precipitates could be observed at the grain boundaries, as indicated in Fig. 4-34 d. The initially extremely regular nanolamellae became corrugated after holding for about 2400 s at 500°C. This distortion in the nanolamellar structure became greater after holding for about 3800 s (Fig. 4-36 a); then the nanolamellar structure was consumed by a new structure which is bright in BF image (Fig. 4-36 b), the bright area increased (Fig. 4-36 c) and finally consumed the grain with the nanolamellar structure (Fig. 4-36 d). However, the initially formed small spherical precipitates could still be seen clearly after the disappearance of the nanolamellae. The SADPs from the grain with corrugated lamellae

(Fig. 4-36 a) and the grain after the nanolamellae was consumed (Fig. 4-36 d) showed a difference in the intensity distribution of the spots.

Further microstructural evolution was mainly initiated by precipitation at the grain boundaries (Fig 4-37 a and b) followed by heterogeneous or homogenous nucleation of new phases (Fig 4-37 c & d). The original nanolamellar structure was thus finally transformed to a multiphase structure.

Fig.4-34 Overall coarsening process of nanolamellar structure in a cobalt based alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ in-situ annealed at 500°C. The holding time is about (a) 0 s, (b) 400 s, (c) 2500 s and (d) 7000 s.

Fig. 4-35 Spherical precipitates and growth. (a) 650 s, (b) 1100 s, (c) 3700 s and (d) 5300 s. The white arrows refer to the fine precipitate. The dashed lines show the waviness of the grain boundary.

Fig. 4-36 Distortion, disappearance of nanolamellae and corresponding SADP. (a) 3800 s, (b) 5000 s, (c) 5400 s and (d) 5900 s. The arrows refer to the corrugation of the nanolamellae. The dashed lines circle the area becoming bright in contrast.

Fig. 4-36 Distortion, disappearance of nanolamellae and corresponding SADP. (a) 3800 s, (b) 5000 s, (c) 5400 s and (d) 5900 s. The arrows refer to the corrugation of the nanolamellae. The dashed lines circle the area becoming bright in contrast. (Continued)

Fig. 4-37 Further transformation after disappearance of nanolamellar structure. (a) 6350 s, (b) 6550 s, (c) 7800 s and (d) 8150 s.

4.2 Processing of Co based amorphous alloys by mechanical alloying

Mechanical alloying was carried out to process the amorphous alloys with nominal composition $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$, as a counterpart study of melt spun $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy. The as milled products were characterized using SEM, XRD, DSC and VSM to explore the alloying and amorphization process. The amorphous alloys were successfully formed after 20 h milling, these alloys exhibited good soft magnetic properties. Annealing was also carried out, the magnetic properties of the annealed samples were tested using VSM.

4.2.1 Alloying process and amorphization

Fig. 4-38 shows the morphological evolution during MA of powders with nominal composition $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$. After 100 min of milling, the mixture of elemental powders firstly formed large particles, many fine particles can be clearly observed within

Fig. 4-38 Morphologies of as milled powders. Nominal composition: $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$.

Fig. 4-39 Morphologies of as milled powders. Nominal composition: $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$.

each of the large particles (Fig. 4-38 a). After a short time of further milling, the surface of the particles became smooth and they were more uniform in size (Fig. 4-38 b). Sharp sheared surfaces were then observed in some of the particles (Fig. 4-38 c), at this stage the particle size was less than $10\ \mu\text{m}$ and agglomeration of particles occurred. At a later stage of milling time, the particles were layered and a number of holes were observed in these particles (Fig. 4-38 d). Powders without Fe and Ni additions, with a nominal composition of $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ showed a similar morphological evolution process (Fig. 4-39). From Fig. 4-39 (b), it can be seen that particles are embedded with many fine particles and have a large uniform size of about $20\ \mu\text{m}$, which is different from Fig. 4-38 (b) of the particles containing Fe and Ni. During the retrieval of the powders, it was found that sticking of the particles to the vials was serious after 20 h of milling.

The XRD results of the as milled powders showed a broad hump with the 2θ in the range of $40\sim 50$ degree (Fig. 4-40 and Fig. 4-41). The h.c.p. Co phase was also detected in

the 5 h as milled $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ powders (Fig. 4-40 a) and 5 h, 10 h and 20 h as milled $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ powders (Fig. 4-41 a, b and c), which showed broad peaks at 41.7, 44.8, 47.6 and 76.0 degrees.

Fig. 4-40 XRD results of as milled powders with nominal composition $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$. The arrow refers to the h.c.p Co phase.

Fig. 4-41 XRD results of as milled powders with nominal composition $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$. The arrows correspond to h.c.p Co peaks.

4.2.2 Thermal properties of MA Co based alloy powders

The as milled powders were characterized using DSC to study their thermal properties. Fig. 4-42 and Fig. 4-43 show the DSC results of the as milled $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ powders and $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ powders respectively. For both compositions, a large exothermal hump was observed in the DSC result of 150 min as milled powders during dynamic heating. 20 h, 40 h and 80 h as milled $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ powders showed exothermal peaks at 537 °C, 524 °C and 511 °C respectively; 20 h, 40 h and 80 h milled $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ powders showed exothermal peaks at 538 °C, 512 °C and 501 °C respectively. In Fig. 4-42, a small exothermal peak at 657°C can also be seen for 150 min milled $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ powders.

Fig. 4-42 DSC results of as milled $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ powders. Heating rate: 20 °C/min.

Fig. 4-43 DSC results of as milled $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ powders. Heating rate: $20\text{ }^{\circ}\text{C}/\text{min}$.

4.2.3 Magnetic properties

The as milled and heat treated powders were tested using the VSM. Fig. 4-44 and Fig. 4-45 are the saturation magnetization and coercivity of as milled $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ powders. For both compositions, the saturation magnetization (M_s) decreased with increasing milling time; the coercivity (H_c) increased initially with milling time then decreased. Both compositions showed a peak of H_c after 150 min of milling, with values of 12000 A/m and 13000 A/m respectively for $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ powders. The lowest coercivity obtained in the as milled powders are 1000 A/m and 890 A/m for $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ powders. The magnetic properties of sample heat treated at $350\text{ }^{\circ}\text{C}$, $400\text{ }^{\circ}\text{C}$, $450\text{ }^{\circ}\text{C}$ and $500\text{ }^{\circ}\text{C}$ for 2 h are shown in Fig. 4-46 and Fig. 4-47. It is interesting to note that M_s decreased with increasing annealing temperature while H_c increased considerably for mechanically alloyed powders of both nominal compositions.

Fig.4-44 Saturation magnetization and coercivity variation with milling time of as milled Co₆₅Si₁₅B₁₄Fe₄Ni₂ powders. Points connected by a dashed line are from bulk sample.

Fig. 4-45 Saturation magnetization and coercivity variation with milling time of as milled Co₇₁Si₁₅B₁₄ powders.

Fig. 4-46 Variation of M_s and H_c with annealing temperature of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ MA alloy.

Fig. 4-47 Variation of M_s and H_c with annealing temperature of $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ MA alloy.