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4. 3 Nanocrystallization behavior of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ HiTperm alloy

The copper free HiTperm $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy exhibited a nanocrystallization behavior upon annealing. The crystallization process in this alloy, the characteristics of the nanocrystals formed, thermal stability, magnetic properties of both as spun of annealed samples were studied in detail using DSC, electrical resistivity, XRD, TEM, HRTEM and VSM. Quantitative analysis was carried out for the first time in this work.

4.3.1 Physical properties variation during the crystallization

Dynamic DSC and electrical resistivity measurements were conducted to characterize the crystallization behavior of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous alloy (Fig. 4-48 and Fig. 4-49). During the dynamic heating, two sets of exothermic peaks were observed (Fig. 4-48), corresponding to primary crystallization and secondary crystallization events of the $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous alloy. Consistent with the DSC results, the dynamic electrical resistivity drops sharply in the temperature range of 480 °C~515 °C and 690 °C~715 °C (Fig. 4-49). Fig. 4-50 is the differential curve of the electrical resistivity verse

Fig. 4-48 Dynamic DSC results of melt-spun amorphous $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ magnetic alloy.

Fig. 4-49 Electrical resistivity variation with temperature of melt-spun amorphous $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ magnetic alloy at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$. p_0 is the electrical resistivity of melt-spun amorphous $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ magnetic alloy at room temperature. The dotted lines are the fitting curves of the electrical resistivity v/s temperature for amorphous phase and crystalline phase respectively in $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy.

Fig. 4-50 Differential curve of electrical resistivity v/s temperature matches well with the DSC curve.

Table 4-7 Values from dynamic DSC and electrical resistivity experiment of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$.

Type	Heating rate	Primary crystallization				Secondary crystallization	
		Peak temperature	Beginning temperature	Ending temperature	Heat transferred	Peak temperature	Heat transferred
DSC	5 °C/min	495.0 °C	473.5 °C	514.0 °C	93.6 J/g	684.0 °C	16.8 J/g
	10°C/min	504.5 °C	481.0 °C	525.0 °C	94.2 J/g	694.0 °C	13.8 J/g
	20°C/min	515.5 °C	491.0 °C	548.0 °C	91.0 J/g	704.0 °C	10.5 J/g
Resistivity measurement	10°C/min	497.0 °C	475.0 °C	518.0 °C	-----	697.0 °C	-----

temperature together with the DSC curve of heating rate 10 °C/min; the two curves matched well with each other. The values from dynamic DSC and resistivity measurements are listed in Table. 4-7.

Isothermal electrical resistivity measurements were carried out at temperatures 450 °C, 465 °C and 485 °C (Fig. 4-51). At all the three isothermal temperatures, the electrical resistivity decreased monotonically with holding time: initially the resistivity decreased sharply and at a later stage it decreased gradually. The slope of the decrease of resistivity depended on the holding temperatures.

Fig. 4-51 Electrical resistivity variation with time at temperatures (a) 450 °C, (b) 465 °C and (c) 485 °C of melt-spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloys. ρ_0 is the electrical resistivity melt-spun amorphous $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ magnetic alloy at room temperature.

From the electrical resistivity curve, the temperature dependence of resistivity of the melt spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous alloy and of the final crystallization products can be determined by curve fitting (Fig. 4-49). For the temperature range of $300\text{ }^\circ\text{C} < T < 600\text{ }^\circ\text{C}$, the relative electrical resistivity of amorphous $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ can be expressed as

$$\rho_a(T) = 2.64 \times 10^{-3} T + 1.005 \quad (4-1);$$

the relative electrical resistivity of the crystallization products can be expressed as

$$\rho_c(T) = 9.58 \times 10^{-3} T + 0.099 \quad (4-2).$$

4.3.2 XRD results

The samples heat treated at $450\text{ }^\circ\text{C}$ and $600\text{ }^\circ\text{C}$ were studied by XRD to determine the phases obtained by crystallization (Fig. 4-52 and Fig. 4-53). For $450\text{ }^\circ\text{C}$ heat treated samples, only broad peaks corresponding to α -(Co, Fe) crystalline phase were observed (Fig. 4-52). The crystalline peaks had higher intensity for longer heat treatment time. For the $600\text{ }^\circ\text{C}$ heat treated samples, α -(Co, Fe) phase as well as the iron oxide phase were

Fig. 4-52 XRD results of samples heat treated at $450\text{ }^\circ\text{C}$ for (a)20 min, (b)60 min and (c) 120 min.

Fig. 4-53 XRD results of samples heat treated at 600 °C for (a) 8 h and (b) 24 h.

detected using XRD (Fig. 4-53). The crystalline peaks were sharp in samples heat treated at 600 °C (Fig. 4-53).

4.3.3 Morphological evolution

The samples heat treated at temperatures of 400 °C, 420 °C, 450 °C and 465 °C were found from TEM observations to be nanostructured. Fig. 4-54 and Fig. 4-55 showed the nanocrystallization process of samples heat treated at 400 °C and 420 °C respectively. From the initial amorphous phase, sparse nanocrystals of about 10 nm in size were firstly observed (indicated in Fig. 4-54 a and Fig. 4-55 a). With longer heat treatment times, both size and density of the nanocrystals increased (Fig. 4-54 b&c and Fig. 4-55 b, c&d). At both 400 °C and 420 °C, a high density of nanocrystals was observed after 240 min heat treatment (Fig. 4-54 d and Fig. 4-55 e). Fig. 4-54 (e) and (f) are the SADPs from samples with a low density of nanocrystals and with a higher density of nanocrystals, showed a diffuse and sharp ring pattern, respectively. From the ring pattern of the SADP (Fig. 4-54 f) was indexed, and the crystalline phase was found to be α -(Co, Fe). The microstructure

Fig. 4-54 Morphological evolution of melt-spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy when heat treated at 400 °C.

The arrows refer to the nanocrystals.

Fig. 4-55 Morphological evolution of melt-spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy when heat treated at 420°C .

The arrows refer to the nanocrystals.

Fig. 4-56 Morphological evolution of melt-spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy heat treated at 450 °C.

Fig. 4-57 Morphological evolution of melt-spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy heat treated at 465 °C.

showed little difference between samples heat treated at 420 °C for 240 min and 420 °C for 480 min (Fig. 4-55 e & f); both showed cluster like crystals. A similar microstructure was also observed in samples heat treated at 450 °C and 465 °C for various heat treatment times (Fig. 4-56 and Fig. 4-57). From Fig. 4-56 and Fig. 4-57, it can be seen that a high

density of nanocrystals were crystallized after a short time of holding at 450 °C and 465 °C (Fig 4-56 a and Fig. 4-57 a). Interestingly, no significant crystal growth or other morphological changes can be observed for longer holding time at these temperatures (Fig. 4-56 b and Fig. 4-57 b).

A high density of nanocrystals were also observed in samples heat treated at a high temperature of 600 °C (Fig. 4-58 a & b). For samples heat treated with holding time less

Fig. 4-58 Morphological evolution of melt-spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy when heat treated at 600 °C and SADPs.

(c)

Fig. 4-59 Morphology of melt-spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy heat treated at 700 °C for 240 min. (a)BF, (b) DF, (c) SADP. From center to edge, the rings (in SADP of (c)) correspond to 1. $(\text{Co}, \text{Fe})_3\text{Zr}$ (400), 2. $(\text{Co}, \text{Fe})_3\text{Zr}$ (331), 3. $(\text{Co}, \text{Fe})_3\text{Zr}$ (422), 4. $(\text{Co}, \text{Fe})_3\text{Zr}$ (511), 5. (Co, Fe) (110) and $(\text{Co}, \text{Fe})_3\text{Zr}$ (440), 6. $(\text{Co}, \text{Fe})_3\text{Zr}$ (620), 7. $(\text{Co}, \text{Fe})_3\text{Zr}$ (533) and (622), 8. $(\text{Co}, \text{Fe})_3\text{Zr}$ (551), 8. $(\text{Co}, \text{Fe})_3\text{Zr}$ (731), 9. $(\text{Co}, \text{Fe})_3\text{Zr}$ (800), 10. (Co, Fe) (200) and $(\text{Co}, \text{Fe})_3\text{Zr}$ (733), 11. (Co, Fe) (211).

4.3.4 Quantitative analysis of crystallization products

Quantitative analysis of the grain size and distribution, nucleation density and volume fraction of crystalline phase was carried out. Fig. 4-60 shows the average grain size: for samples heat treated at 400 °C, 420 °C, 450 °C, an increase in grain size with heat treatment time was observed; for samples heat treated at 465 °C, the average grain size stabilized at about 30 nm; for samples heat treated at 600 °C for 4 h and 8 h, the average grain size was 29 nm and 33 nm respectively. The grain size showed a Gaussian distribution; the grain size distribution of samples heat treated at 450 °C and 600 °C as a function of annealing time are provided in Fig. 4-61 and Fig. 4-62. For longer heat treatment time, the peak position shifted to larger crystal size and the size distribution became narrower. From the thickness measurement, the nucleation density and crystalline volume fraction could be determined (Fig.4-63). Initially the nucleation density is approximate 10^{21} m^{-3} ; after sufficient annealing time, the nucleation density is higher,

Fig. 4-60 Average grain size of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy heat treated over a temperature range of 400 °C to 460 °C for various annealing time.

(a) 450 °C for 20 min

(b) 450 °C for 60 min

(c) 450 °C for 120 min

Fig. 4-61 Grain size distribution of samples heat treated at 450 °C.

(a) 600 °C for 4h

(b) 600 °C for 8 h

Fig. 4-62 Grain size distribution of samples heat treated at 600 °C.

(a)

(b)

Fig. 4-63 (a) Nucleation density and (b) Crystalline volume fraction of melt-spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloys annealed at 400 °C, 420 °C and 450 °C. The two data points are connected only as a guide to the eye.

approximately 10^{22} m^{-3} (Fig. 4-63 a). The crystalline volume fraction increased with an increase in annealing time, especially for samples annealed at 400 °C and 420 °C (Fig. 4-63 b); a linear increase in crystalline volume fraction with annealing time was observed in samples heat treated at 450 °C.

4.3.5 Detailed microstructural analysis

Conventional TEM, HRTEM and CBED techniques were used for a detailed analysis of the microstructure. Fig. 4-64 shows the morphology of crystals for various heat treatment conditions and the corresponding high resolution images. The crystals initially has a relatively regular shape (Fig.4-64 a); then the crystals become irregular with several sharp corners (Fig. 4-64 b); finally the crystals are cluster like with a mean size of 20~30 nm (Fig. 4-64 c). From the corresponding lattice fringes, it can be seen that the crystals with the cluster like features are in fact single crystals. Further evidence is provided in Fig. 4-65, which shows BF images of the crystals and the corresponding CBED patterns. Each CBED exhibits only a single diffraction pattern, indicating that only a single crystal was involved.

4.3.6 Magnetic properties

The as-spun and heat treated samples were tested in VSM. The hysteresis loops of as-spun ribbon and samples heat treated at 600 °C are shown in Fig. 4-66. An increase in coercivity and saturation magnetization as well as a decrease in the squareness of the loop was observed for the sample heat treated at 600 °C for 1440 min. For samples heat treated at lower temperatures or heat treated at 600 °C for shorter times, the coercivity and squareness of the loops are comparable with those of the as spun ribbon (Fig. 4-66). The saturation magnetization and coercivity of samples is listed in Table 4-8. From Table 4-8, an important result is that the saturation magnetization increased considerably after heat

Fig. 4-64 Nanocrystal at different stages and corresponding HRTEM micrographs.

Fig. 4-65 Nanocrystals in the sample annealed at 465 °C for 8 h. (a) nanocrystals and the corresponding CBED with the zone axis [100], (b) nanocrystals and the corresponding CBED, (c) HRTEM of nanocrystal in (b).

Fig. 4-66 Hysteresis loops of as received and samples heat treated at 600 °C.

Table 4-8 Saturation magnetization (M_s) and coercivity (H_c) of as received and heat treated samples

Heat treatment		M_s (T)	H_c (A/m)
Temperature (°C)	Holding time (min)		
As-spun		1.697	210
400	20	1.646	380
	60	1.615	400
	120	1.707	450
	240	1.751	380
420	15	1.731	440
	30	1.737	400
	60	1.705	370
	120	1.709	420
	240	1.796	330
	480	1.836	320
450	20	1.771	330
	60	1.834	310
	120	1.852	320

Table 4-8 Saturation magnetization (M_s) and coercivity (H_c) of as received and heat treated samples.
(Continued)

Heat treatment		M_s (T)	H_c (A/m)
Temperature (°C)	Holding time (min)		
465	20	1.825	330
	30	1.834	250
	60	1.833	280
	120	1.829	320
	240	1.829	330
	480	1.863	370
	960	1.864	300
600	30	1.826	310
	60	1.838	330
	120	1.849	340
	240	1.834	350
	480	1.838	460
	1440	1.883	1750

treatment: the saturation magnetization of the melt spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous alloy was 1.697 T; the samples heat treated at 420 °C for 480 min, 450°C for 120 min and 240 min had a M_s of approximately 1.83 T. The M_s of the sample heat treated at 600 °C for 1440 min was about 1.88 T. The coercivity of the samples did not increase much after heat treatment except for the sample heat treated at 600 °C for 1440 min. The coercivity of the sample heat treated at 600 °C for 1440 min was about ten times of that of the melt spun $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy. Another important correlation is that between magnetic properties and the crystalline volume fraction and average size (Fig. 4-67). Interestingly in Fig. 4-67 (a), the relationship between crystalline volume fraction and saturation magnetization showed a linearly increasing relationship; in Fig. 4-67 (b), the relationship between the average grain size and coercivity showed that the coercivity decreased with an increase of crystal size in the $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy.

Fig. 4-67 (a) Saturation magnetization as a function of crystalline volume fraction. (b) Coercivity as a function of the average crystal size in the $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy.

4.4 Processing of nanocrystalline Co-Fe based magnetic materials by mechanical alloying

Nanocrystalline magnetic alloys $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ has been processed by mechanical alloying in this work. The alloying process, powder morphological evolution during the milling, microstructures of as milled particles, magnetic properties are studied using SEM, EDX mapping, XRD, TEM and VSM. The effects of milling speed, additional elements P and B on the alloying process, powder morphologies are included. The large stress in the as milled powders is tested using DSC. Annealing improved the soft magnetic properties of these MA powders.

4.4.1 Powder morphology evolution of mechanical alloyed $\text{Co}_{50}\text{Fe}_{50}$ powders

The morphology of as milled powders after short milling times is shown in Fig. 4-68. Starting from the initial irregular shaped Fe elemental particles and spheroidal shaped Co particles (Fig. 4-68 a & b), particles with irregular shape and smaller size were observed after 25 min of milling at 300 rpm (Fig. 4-68 c). After milling for 100 min, interestingly, a significant increase of particle size was observed (Fig. 4-68 d & e). Further milling of 200 min decreased the particle size (Fig. 4-68 f).

Fig. 4-69 showed the elemental mapping of the short time as milled $\text{Co}_{50}\text{Fe}_{50}$ powders. From Fig. 4-69 (a) and (b), the maps of elements Fe and Co were well separated for particles milled for 25 min and 50 min. After 100 min of milling (Fig. 4-69 c), it can be seen that the maps of Fe and Co are correlated, some small differences were also observed in these two maps (circled region in Fig. 4-69 c). In Fig. 4-69 (d) of 200 min as milled powders, the two maps are very well correlated.

The morphology of longer time milled powders are shown in Fig. 4-70. It can be seen that there is a decrease in particle size for longer milling time at a milling speed of 300 rpm. The shape of particles appeared to be more equiaxed although the surface features

(a) Pure Fe (un-milled)

(b) Pure Co (un-milled)

(c) 25 min

(d) 50 min

(e) 100 min

(f) 200 min

Fig.4-68 Morphologies of short time as milled $\text{Co}_{50}\text{Fe}_{50}$ powders. Milling speed: 300rpm.

from 5 h to 15 h of milling, but decreased slowly on further milling (Table 4-9). The smallest mean particle size reached was about 3.3 μm after 70 h of milling at 300 rpm for $\text{Co}_{50}\text{Fe}_{50}$ powders.

(a) 5 h.

(b) 10 h.

(d) 20 h.

(f) 40 h.

(g) 50 h.

(h) 70 h.

4.4.2 The effect of alloying elements P and B on powder morphology.

Additional alloying elements P and B have a significant effect on the particle size and morphology. Fig. 4-72 shows the morphology of powders with nominal composition $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ after a short time of milling at 300 rpm. The particle size increased significantly (from less than 10 μm to more than 20 μm) for 25 min to 100 min of milling (Fig. 4-72 a, b&c); after 200 min of milling, the particle size decreased to less than 10 μm (Fig. 4-72 d). For longer time of milling at 300 rpm, the particle size decreased further, the particles became more spherical in shape and more uniform in size. Fig. 4-73 and Fig. 4-74 show the morphology and the size distribution respectively of these particles.

Fig. 4-72 Morphologies of short time as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders. Milling speed: 300 rpm.

Fig. 4-73 Morphology of long time as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders. Milling speed: 300 rpm.

Fig. 4-74 Size distribution of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders as milled at 300 rpm. (Continued)

Mechanical alloying of $\text{Co}_{42.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$ and $\text{Co}_{41.5}\text{Fe}_{41.5}\text{P}_{14}\text{B}_4$ powders was also carried out to investigate the effect of P and B on the processing of Co-Fe based alloys. From 4-75, it can be seen that after 15 h of milling at 300 rpm the $\text{Co}_{42.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$ powders were spheroidal and had a size of less than 5 μm. For the composition $\text{Co}_{41.5}\text{Fe}_{41.5}\text{P}_{14}\text{B}_4$, the particles were initially spheroidal (Fig. 4-75 a&b), later, faceted particles were observed (Fig. 4-76 c).

The average size and size distribution of as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$, $\text{Co}_{42.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$ and $\text{Co}_{41.5}\text{Fe}_{41.5}\text{P}_{14}\text{B}_4$ powders are provided in Table 4-10.

Fig.4-75 Morphology of as milled $\text{Co}_{42.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$ powders. Milling speed: 300 rpm.

Table 4-10 Particle size of as milled powders after different periods of milling.

Composition	Milling time (h)	Size distribution (μm)	Average size (μm)
$\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$	5	1.0 ~14.0	3.2
	10	0.6 ~6.8	2.1
	15	0.6 ~5.6	1.7
	20	0.4 ~5.0	1.5
	50	0.3 ~4.0	1.4
	70	0.3 ~3.5	1.1
$\text{Co}_{42.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$	5	3 ~20	9.4
	10	1 ~5	1.8
	15	1 ~5	1.9
$\text{Co}_{41}\text{Fe}_{41}\text{P}_{14}\text{B}_4$	5	1 ~6	2.6
	10	1 ~9	3.1
	15	0.5 ~10	1.6

-----Results: MA Co-Fe based nanomagnetic alloys -----

4.4.3 Effect of milling speed on the powder size

After 5 h high energy milling to alloy the powders, a low speed of 200 rpm for further milling was used to study the effect of milling speed on the particle size. For $\text{Co}_{50}\text{Fe}_{50}$ powders, the size decreased significantly with an increase in milling time and the particles were more uniform in size and morphology (Fig. 4-77); for $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders, the morphology of particles did not change much and the size decreased slightly with longer milling time (Fig. 4-78). Table 4-11 provides the average size and the size distribution range of 200 rpm milled $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders.

Fig. 4-77 Morphology of 200 rpm as milled $\text{Co}_{50}\text{Fe}_{50}$ particles.

Fig. 4-78 Morphology of 200 rpm as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ particles.

Table 4-11 Particle size and size distribution range of 200 rpm as milled $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders.

Composition	Conditions	Size distribution (μm)	Average particle size (μm)
$\text{Co}_{50}\text{Fe}_{50}$	5 h (300 rpm)+5 h (200 rpm)	1.5 ~16.5	4.9
	5 h (300 rpm)+10 h (200 rpm)	1.5 ~13.0	4.1
	5 h (300 rpm)+15 h (200 rpm)	1.0 ~11.5	3.7
$\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$	5 h (300 rpm)+5 h (200 rpm)	0.8 ~12.0	2.9
	5 h (300 rpm)+10 h (200 rpm)	0.6 ~12.4	2.9
	5 h (300 rpm)+15 h (200 rpm)	0.8 ~13.0	2.8

4.4.4 XRD results

Fig.4-79 XRD results of $\text{Co}_{50}\text{Fe}_{50}$ powders as milled at 300 rpm for different milling time.

Fig. 4-79 shows the XRD results of $\text{Co}_{50}\text{Fe}_{50}$ powders milled for different milling time at 300 rpm. From Fig. 4-79, it can be seen that when the milling time is less than 100 min, the Fe and Co peaks can be distinguished; but after 200 min of milling, only one set of peaks corresponding to the formation of CoFe compound was observed; a change in position of XRD peaks was observed for powders milled for 100 min and 200 min. For 5 h to 70 h of milling, the XRD results of $\text{Co}_{50}\text{Fe}_{50}$ powders did not vary significantly; no further broadening of peaks was observed.

Fig. 4-80 XRD results of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders as milled at 300 rpm for different milling time.

The XRD results of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders are shown in Fig. 4-80. The Co and Fe peaks can be readily distinguished in the XRD results of 100 min milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders. Beyond 200 min milling, only one set of peaks corresponding to the α -(Co, Fe) phase was observed. The broadening of peaks occurred in the XRD results of 5 h to 70 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders (Fig. 4-80 f-l). For 40 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders, a hump was observed below the XRD peak (circled in Fig. 4-80 k).

Fig. 4-81 shows the XRD results of 300 rpm 15 h milled $\text{Co}_{41.5}\text{Fe}_{41.5}\text{P}_{14}\text{B}_4$ and $\text{Co}_{42.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$ powders. It can be seen that the h.c.p Co phase could be detected in the $\text{Co}_{41.5}\text{Fe}_{41.5}\text{P}_{14}\text{B}_4$ powders.

Fig. 4-81 XRD results of 300rpm 15 h milled (a) $\text{Co}_{41.5}\text{Fe}_{41.5}\text{P}_{14}\text{B}_4$ and (b) $\text{Co}_{42.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$ powders.

4.4.5 TEM microstructural observations

Fig. 4-81 (a)-(d) shows the bright field TEM micrographs of $\text{Co}_{50}\text{Fe}_{50}$ particles milled at 300 rpm for various milling times. A banded microstructure was observed in the 5 h milled particles (Fig. 4-82 a); after longer milling time, the banded structure became more random and finer. The SADP and dark field micrograph in Fig. 4-82 (e) shows that the CoFe phase was formed in 5 h of milling and the banded microstructure was a result of

(a) 5 h

(b) 10 h

(c) 20 h

(d) 70 h

(e) SADP and dark field image of (a) at the condition of as circled.

Fig. 4-82 TEM images of $\text{Co}_{50}\text{Fe}_{50}$ particles as milled at 300 rpm for different milling time.

Table 4-12 Compositions of neighboring bands in 5 h as milled particlers determined using EDX attachment in TEM.

Powder	Neighboring bands	Composition	
		Fe (at. %)	Co (at. %)
1	A	46	54
	B	50	49
	C	50	49
2	A	45	55
	B	47	53
	C	45	55
3	A	50	50
	B	36	64
	C	34	66
	D	40	60

texturing. Using EDX attachment of TEM, the compositions between two neighboring bands were found to be similar (Table 4-12).

The banded microstructure was also observed in the 5 h as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ particles (Fig. 4-83 a). It disappeared in the 10 h milled particles; in these particles, spheroidal nanocrystalline with a size of about 30 nm was observed instead (Fig. 4-83 b). Longer time of milling at 300 rpm reduced the size of the nanocrystals to less than 20 nm (Fig. 4-83 c and d). The SADP of 5 h and 10 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders are shown in Fig. 4-83 (e) and (f), respectively. In Fig. 4-83 (e), a weak texture effect was observed. This texture effect was not observed in Fig. 4-83 (f).

4.4.6 Thermal properties of MA $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders

The DSC results of MA $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders showed large stress relaxation humps. Fig. 4-84 shows the DSC results of the $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders milled at 300 rpm for 70 h. The DSC result of 70 h $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders also exhibited a small exothermal peak at 445°C.

Fig. 4-83 TEM images of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders as milled at 300 rpm for different milling time.

Fig. 4-84 DSC results of 300rpm, 70 h milled $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders.

4.4.7 Magnetic properties

Fig. 4-85 and Fig. 4-86 show the variation of magnetic properties with milling time for the 300 rpm as milled $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders respectively. For the $\text{Co}_{50}\text{Fe}_{50}$ powders, the magnetization increased with milling time for milling time less than 10 h and it did not change much with the further milling; the coercivity appeared to increase significantly with milling time (Fig. 4-85). Interestingly, for the $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders, the M_s increased with milling time for up to 70 h of milling; the coercivity increased significantly after 20 h of milling, it then decreased with milling time on further milling. As expected, the H_c of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders were larger than those of $\text{Co}_{50}\text{Fe}_{50}$ powders after the same milling time.

The magnetic properties of milled samples after annealing at 350 °C, 400 °C, 450 °C and 450 °C for 2 h are shown in Fig. 4-87 and Fig. 4-88. Interestingly, for both MA $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders, the coercivity decreased significantly after annealing. From Fig. 4-87, it can be seen that the coercivity of MA $\text{Co}_{50}\text{Fe}_{50}$ powders decreased with an increase in annealing temperature; the magnetization stabilized at the

Fig. 4-85 Magnetic property variation with milling time in 300 rpm as milled $\text{Co}_{50}\text{Fe}_{50}$ powders.

Fig. 4-86 Magnetic property variation with milling time in 300 rpm as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders.

high value 2.2 T for 20 h and 70 h milled $\text{Co}_{50}\text{Fe}_{50}$ powders; the magnetization of 5 h (300 rpm) + 15 h (200 rpm) milled powders increased with annealing temperature. The variation of magnetic properties with annealing temperature was complex in the MA $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders (Fig. 4-86). The magnetic properties of 20 h milled and 5 h (300 rpm)+15 h (200 rpm) milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders were similar after annealing at 400

°C, 450 °C and 500 °C for 2 h. For 70 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders, a minimum coercivity of 970 A/m was obtained after annealing at 400 °C.

Fig. 4-87 Magnetic property of annealed (a) $\text{Co}_{50}\text{Fe}_{50}$ and (b) $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ MA powders.

Chapter 5 Discussion

In this chapter, the results obtained and presented in Chapter 4 will be discussed.

The crystallization behavior of metallic glass $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ will be discussed, including the nature of the phase transformation process, a detailed microstructural analysis, the mechanism of nanolamellar structure formation, the coarsening of the nanolamellar structure and the correlation between microstructure and magnetic properties. The mechanical amorphization process of alloys with compositions based on the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ composition will be analyzed. The properties of these mechanically alloyed amorphous alloys will be compared with those of the melt spun alloys.

The nanocrystallization behavior of Cu free HiTperm alloy $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ will be discussed. The nucleation of a high density of nanocrystals, the slow growth rate of these nanocrystals and the precipitation of secondary phases in this Cu free HiTperm alloy will be discussed and compared with the Cu containing HiTperm alloy. Nanocrystalline Co-Fe based alloys were also processed by mechanical alloying. The mechanical alloying process, the mechanism of the nanostructure formation and the modification of microstructure by alloying elements will be discussed in the light of the results in Chapter 4. At the end of this chapter, a comparison of the phase transformations in mechanically alloyed and melt spun alloys will be made, and the correlation between magnetic properties and microstructure will be discussed.

5.1 Crystallization behavior of amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy

Amorphous alloys, which are in a metastable state, can crystallize when heated or held at elevated temperature for sufficient time. The crystallization behavior of amorphous alloys can vary from each other; the microstructures obtained through crystallization can be nanocrystals in an amorphous matrix, dendrites, equiaxed or eutectic structures, depending on the composition and treatment conditions. The amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy showed a complex crystallization process. It formed a nanolamellar structure after conventional heat treatment. In this section, the crystallization behavior of this alloy will be discussed. The characteristics of nanolamellar structure and subsequent transformations are discussed. In-situ thin foil crystallization, which induced the formation of nanocrystalline microstructure, is also included.

5.1.1 Dynamic crystallization characteristics of the amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy

The DSC technique is the most frequently used method to study the crystallization behavior of metallic glasses. From the DSC results (Fig. 4-1), two exothermal reactions were observed during the dynamic heating of the initially amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy. The first reaction occurred in the temperature range of 532~546 °C, 538~558 °C and 544°C~571 °C at a heating rate of 5 °C/min, 10 °C/min and 20 °C/min respectively (Table 4-1). It is clear that the starting temperature and temperature range of the reaction increased with the increasing heating rate. The heat involved in this reaction was about 86 J/g. The second exothermal reaction event occurred at around 650 °C, the heat involved in this reaction was small. Consistent with the DSC results, the electrical resistivity drops at the temperatures of the two exothermal reaction events. The temperature range of the reaction from electrical resistivity measurement was very close to that obtained from DSC analysis.

The crystallization of metallic glass usually follows one of three modes of reaction: polymorphous, primary and eutectoid (or eutectic if metallic glass is considered as quenched liquid melt) [137-138]. The two step exothermal reaction process of metallic glass is generally considered to be a primary crystallization mode [137-138, 161, 166]. From the results of microstructural observations (section 4.1.2), the initial crystallization product is large grains within which a nanolamellar structure is observed. There is no feature of primary crystallization in this $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ metallic glass. The crystallization of metallic glass $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ was thus polymorphous.

The Kissinger method [222-223] is often used to determine the activation energy of reaction from dynamic DSC results [19, 137-139]. Using this method by plotting $\ln(\phi/T_p^2)$ against $(1/T_p)$ and by calculation of the slope (E_x/k) of the line (Fig. 5-1), the activation energy of crystallization was determined to be 7.1 ± 0.3 eV/atom; that of the second exothermal reaction was 4.9 ± 0.9 eV/atom. Here ϕ is the heating rate of DSC experiment, T_p is the corresponding peak temperature of reaction, E_x is the activation energy of reaction. Compared to Finemet, HiTperm amorphous precursors and most Fe based metallic glasses, this activation energy of the crystallization of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ is

Fig. 5-1 Activation energy of (a) crystallization and (b) second exothermal reaction of metallic glass $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ using Kissinger method.

quite large; in Finemet and HiTperm amorphous precursors, the activation energies are about 4 eV/atom and 3.5 eV/atom respectively [19]. In some compositions of Co-Si-B metallic glasses, large activation for crystallization was also observed [161], e.g., the activation energy was 8.75 eV/atom for crystallization of metallic glass $\text{Co}_{70}\text{Si}_9\text{B}_{21}$ and 6.76 eV/atom for metallic glass $\text{Co}_{70}\text{Si}_{15}\text{B}_{15}$. The activation energy is known to be related to the migration of atoms [224]. The large activation energy of crystallization in $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy indicated that the reaction is highly sensitive to temperature.

The crystallization product related to the first exothermal reaction was tentatively interpreted to be a multi-phase mixture of Co_2Si , Co (hcp), Co(fcc) and Co_3B_2 from XRD results (Fig. 4-4). However, after TEM characterization of many samples, it was instead found that the crystallization product possessed a C base centered orthorhombic crystalline phase with $a=0.74$ nm, $b=1.07$ nm and $c=0.77$ nm. This will be discussed in more detail in section 5.1.3. The second exothermal reaction corresponded to the formation of Co_2B , Co_4B , Co_2Si and h.c.p Co phases from the XRD results (Fig. 4-4).

Since electrical resistivity of bulk material depends on both the nature of the phases it contains and their distribution [225], the resistivity measurement showed more details of the structural variation than DSC. Several small variations can be observed in the resistivity curve besides the two large electrical resistivity drops during the dynamic heating (Fig. 4-2). At about 220 °C, the temperature coefficient of resistivity decreased slightly; this temperature was the Curie temperature of the amorphous alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ [197]. Before the drop of the crystallization event, a plateau of electrical resistivity was observed at a heating rate of 10 °C/min but not at a heating rate of 20 °C/min, which may be related to structural relaxation [133-134] or phase separation in the amorphous state [137, 207, 226]. In Tsai's investigation of effect of annealing on the magnetic properties of metallic glass 2714A [197], annealing at 340 °C~490 °C for 30 min improved the initial permeability. Tsai attributed the improvement to nanocrystalline formation. However, from our TEM microstructural observation, for samples heat treated

at 480 °C for less than 180 min, no crystalline phase was formed. The improvement of the soft magnetic properties of samples annealed at the temperature range of 340 °C~490 °C could be due to the irreversible relaxation or phase separation in amorphous state since the increase of the slope in resistivity v/s temperature was obvious at this temperature range, which corresponded to short range ordering of atoms before crystallization; higher heating rate can however bypass this process. In the resistivity v/s temperature curve, it can also be seen that: (a) the decrease of resistivity due to the crystallization is less at a heating rate of 20 °C/min than at a heating rate of 10 °C/min; (b) there is a small hump after crystallization in the temperature range of 550 °C~570 °C at a heating rate of 10 °C/min; and (c) the electrical resistivity drops sharply again at about 750 °C during heating. These variations are due to the crystallization products and the subsequent transformations at elevated temperatures.

From the above analysis, a complex crystallization process and other transformations is expected in the amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ magnetic alloy.

5.1.2 Isothermal crystallization behavior and overall morphological evolution in the amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy.

The study of kinetics of crystallization process is effective in understanding the crystallization behavior and provides a method for modeling of crystallization.

Isothermal electrical resistivity measurements were carried out to study the isothermal crystallization behavior of the amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy at 500 °C and 510 °C (Fig. 4-3). For both temperatures, the resistivity variation with time showed that the resistivity initially increases at the beginning of isothermal heat treatment; after a sharp decrease, it increases again and finally stabilizes. This resistivity behavior is different from general crystallization from amorphous phase, where the resistivity continuously decreases because the resistivity of the ordered alloy is lower than the disordered one of same composition. It again indicated a complex crystallization process of this amorphous alloy, which was consistent with dynamic electrical resistivity observations.

A better understanding of the resistivity variation with holding time can be obtained from TEM investigations of the microstructure and its evolution with time. Fig. 4-9 indicates: (a) a number of large crystalline precipitates were observed after 10 min; (b) crystallization was almost complete after 30 min; (c) a number of small precipitates were observed at the grain boundaries after 80 min; (d) these small precipitates increased in number, they were also observed within the grains.

The increase of resistivity in the early stages was thus associated with the nucleation of the crystalline phase, which may cause variation of the structure factor [227] in amorphous state. The structure factor depends on the correlation between the atomic positions, it directly affects the resistivity of materials. Such an unusual increase in resistivity before crystallization was also previously observed in the amorphous alloys $\text{Co}_{70}\text{Si}_9\text{B}_{21}$ and $\text{Ni}_{70}\text{Si}_9\text{B}_{21}$ [161]. In the case of Finemet amorphous precursor $\text{Fe}_{73.5}\text{Si}_{13.5}\text{B}_9\text{Nb}_3\text{Cu}_1$, an increase in resistivity was also observed after nanocrystallization of the Fe (Si) phase during dynamic heating; this increase was due to the large temperature coefficient of resistivity in nanocrystalline Fe (Si) phase [228]. Since in our investigations, the increase in resistivity was observed for isothermal conditions, the temperature coefficient of resistivity would have no effect on the resistivity evolution.

The decrease of resistivity at later stages was due to the crystallization of the amorphous alloy. When only a small amount of crystals formed, the crystals which have relatively lower resistivity were isolated by the amorphous matrix; therefore the resistivity did not decrease dramatically in the early stage of crystallization. When the volume fraction of crystals was large enough to form a continuous conduction path, the conduction will be dominated by these crystals and the resistivity will decrease continuously with increasing amount of the lower resistivity phase. It can also be seen that the crystalline product was not a good conductor and has a resistivity close to the initial amorphous phase.

Fig 5-2 Co-Si-B ternary phase diagram [229]. (a) at 727°C, (b) vertical section of 15.0 at.% B. Similar composition to $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ is indicated.

The second increase in resistivity after crystallization was mainly due to precipitation of secondary phases at grain boundaries and within the grains. This is because the initial crystalline phase was not the final equilibrium phase. For an alloy composition close to $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$, the equilibrium phases are Co_2Si , Co_2B and h.c.p. Co, from the ternary phase diagram in Fig. 5-2[229]. Grain boundaries and other defects, which have higher energy, will be nucleation sites for formation of these equilibrium phases. The precipitation affected the resistivity by: (a) it produced more interfaces and (b) it caused solute redistribution which led to an increase in resistivity.

The difference in variation of the resistivity at 500 °C and 510 °C is attributed to competition between nucleation, crystallization and precipitation of secondary phases. From a comparison of the two curves in Fig. 4-3, it is clear that the crystallization is very sensitive to temperature as expected from the high activation energy for crystallization obtained from the DSC results.

The investigation of isothermal crystallization behavior of amorphous alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ was also carried out at 530 °C, 560 °C and 600 °C.

Similar to the crystallization behavior at 500 °C, large crystals were first crystallized from the amorphous phase at 530 °C and these large crystals dominated the

microstructure after heat treatment for 5 min (Fig. 4-11 a). The reaction is fast at 530 °C compared to that at 500 °C. After only 30 min of heat treatment at 530 °C (Fig. 4-11 b) a large volume fraction of fine precipitates was observed, while at 500 °C at least 160 min is required to obtain this volume fraction of precipitates. The microstructure then developed into a heterogeneous microstructure (Fig. 4-11 c-f). After heat treatment at 530 °C for 960 min (Fig. 4-11 f), the heterogeneous microstructure (later shown to be result of coarsening of the lamellar structure) dominated the microstructure. At 560 °C, the transformation process was even faster than at 530 °C, for samples heat treated at 560 °C for 10 min (Fig. 4-12 a), a large volume fraction of fine precipitates were observed along with large grains. The heterogeneous microstructure was the major constituent of the microstructure for samples heat treated for 60 min at 560 °C (Fig. 4-12 b), it entirely consumed the initial grains after 240 min of annealing (Fig. 4-12 c). The heterogeneous microstructure underwent further coarsening after heat treatment for longer time (Fig. 4-12 d). The sample heat treated at 600 °C exhibited an equiaxed multiphase mixture (Fig. 4-13). These equiaxed grains were produced by coarsening of the heterogeneous microstructure. With longer time of heat treatment at 600 °C or heat treatment at higher temperatures, the equiaxed grains increased in size (Fig. 4-13 b, Fig. 4-14 and Fig. 4-15) and formed a network of equilibrium crystalline phases.

XRD results reflected this transformation process. From the broad hump (Fig. 4-5 a) corresponding to the amorphous phase, some weak peaks were observed in samples heat treated for 10 min (Fig. 4-5 b). The XRD peaks of the crystalline phase became stronger for longer heat treatment time at 500 °C (Fig. 4-5 b-d). The crystalline phase was found to be an orthorhombic structure with $a=0.74$ nm, $b=1.07$ nm and $c=0.77$ nm. From detailed TEM characterization, the crystals were found to consist of fine nanolamellar structure with wavelength of about 10 nm (see section 4.1.4). The XRD results of samples heat treated at 530 °C for 5 min, 30 min, 240 min and samples heat treated at 500 °C for 30 min, 60 min and 160 min did not show significant difference (Fig. 4-6 a-c and Fig. 4-5 c-

e), although TEM results showed that fine precipitates formed in samples heat treated at 500 °C for 160 min as well as at 530 °C for 30 min, and that a heterogeneous microstructure formed in samples heat treated at 530 °C for 240 min. This is because the intensity of XRD peaks depends on the volume fraction of phases and other factors such as grain size and defects. The relative intensity of the XRD peaks changed significantly in samples heat treated at 530 °C for 480 min and 960 min as well in samples heat treated at 560 °C for 60 min and 120 min. This change in the XRD results corresponded to the formation of a metastable Co_3Si phase (not included in the XRD database) from TEM characterization of the sample. (The details of formation this metastable phase will be discussed in section 5.1.5.) The XRD data showed significant change for samples heat treated at 560 °C for 240 min and 960 min, which was due to further transformation of metastable Co_3Si phase into equilibrium phase Co_2Si , Co_2B and Co phases.

The morphological evolution during heat treatment of amorphous alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ can thus be summarized in the block diagram in Fig. 5-3.

Fig. 5-3 Microstructural evolution and phases developed of metallic glass $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ underwent conventional heat treatment. The orthorhombic phase is a C base centered orthorhombic phase with $a=0.74$ nm, $b=1.07$ nm and $c=0.77$ nm.

5.1.3 Interesting nanolamellar structure and the crystallographic characteristics.

Crystallization from amorphous precursors differs from conventional solidification. It can yield new structures such as nanoprecipitates in an amorphous matrix [19] and quasicrystals [152]; such novel materials are of both scientific and technological interest. In this cobalt based amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy, an interesting and novel nanolamellar structure was obtained for the first time by crystallization using conventional heat treatment (Fig. 4-16). This nanolamellar structure is a new member of nanostructures [19, 137, 154] formed by crystallization from amorphous precursors. It was observed within all the large grains crystallized from amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy: the nanolamellar structure formed in amorphous matrix (Fig. 4-16 a) and appeared within all the large grains when amorphous phase fully crystallized (Fig. 4-16 b), much of the nanolamellar morphology was retained after part of large grains was consumed by precipitation at grain boundaries and heterogeneous microstructure (Fig. 4-16 c).

The composition of the phase with the nanolamellar morphology was close to that of the original amorphous matrix since these crystals were the only constituent in samples after crystallization was completed, e.g., after heat treatment at 500 °C for less than 60 min and 530 °C for 5 min. HRTEM of the nanolamellar structure (Fig. 4-17 a and b) showed no discernible lattice mismatch between the neighboring lamellae, indicating that the nanolamellae did not consist of a two crystal mixture. The EELS mapping (Fig. 4-20) of the lamellar structure showed that phase separation into boron rich and boron lean regions occurred. Since the XRD results of samples with this nanolamellar crystal feature (section 4.1.2) and the composition did not match the phases from known crystals [230] including elemental phases Co, Si, B and compounds Co_xSi ($x=1, 2, 3$), CoSi_2 , Co_3Si_2 , BCo_x ($x=1, 2, 3, 4$) and BCo_5Si_2 , the crystal with nanolamellar structure is considered to be a new crystal phase.

Kikuchi maps, SADP and CBED were used to determine this crystal structure, including the crystal type and crystal parameters. From Kikuchi map observations and

SADPs (Fig. 4-18), this 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. The $(2\ 0\ 0)$, $(0\ 2\ 0)$ and $(0\ 0\ 1)$ planes are the mirror planes (Fig. 4-18 a). The SADPs from zone $[1\ 0\ 0]$, $[0\ 1\ 0]$ and $[0\ 0\ 1]$ are shown in Fig. 4-18 (b) of DPs 1, 3 and 5; it is obvious they match well with each other. CBED from the zones $[1\ 0\ 0]$ and $[0\ 0\ 1]$ shows a $2mm$ BF symmetry (Fig. 4-19 a

arrays of satellite reflection spots can be observed. The occurrence of spot arrays indicated that the composition modulation in this crystal could be square rather than sinusoidal. Thin multilayer structure can also give rise to spot arrays [218].

5.1.4 Thermodynamic explanation for the formation of the nanolamellar structure.

Phases formed in any material depend on composition and processing conditions. For solidification from melt, the cooling rate usually plays a significant role in altering the products since it determines the degree of undercooling and affects nucleation and growth process. For metallic glasses, which are generally prepared by rapid solidification techniques, the microstructures can be further modified by crystallization at large undercooling and slow diffusion. Crystallization is a successful technique to process nanostructures from amorphous precursors [19, 137, 154]. This nanolamellar structure formation by crystallization of the amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy after a simple heat treatment can be related to alloy composition, atomic configuration and diffusion, which allowed new crystal formation and spinodal decomposition.

Crystallization of amorphous alloy is driven by the free energy difference between amorphous phase and appropriate crystalline phase(s) [137]. Fig. 5-3 schematically illustrates the possible free energy difference between the metallic glass and the equilibrium phases Co_2B and Co_2Si (the Co phase was not included in order to simplify the calculation and explanation). The M phase in Fig. 5-3 represents a metastable phase, which corresponds to the crystal with the nanolamellar structure. To determine the crystallization product(s) implies consideration of kinetic factors. There are two cases: formation of metastable phase followed by spinodal decomposition or formation of eutectic phases.

(a) Formation of metastable phase. Since the crystal with nanolamellar structure dominates the microstructure of crystallization product (no other phase was observed except for a small volume fraction of fine precipitates at grain boundaries), a reasonable assumption is that the metastable phase has the same composition as the amorphous matrix, i.e., the

Fig. 5-4 Schematic free energy v/s composition curve for amorphous alloy, crystal with nanolamellar structure (M) and equilibrium eutectic phases.

formation of this metastable phase is a polymorphic transformation. According to nucleation theory [224], the critical radius of nucleation r_c is

$$r_c = -2\gamma_{M-G} / \Delta G_{v-M} \quad (5-1)$$

γ_{M-G} is the interfacial energy of metastable phase and metallic glass; ΔG_{v-M} is the volume free energy change from metallic glass to the metastable crystal, which corresponds to ΔG_1 in Fig.5-4. From our observations, the crystal size is in the submicron range when sparse crystals are precipitated from the metallic glass (Fig 4-10 & Fig 4-16 a). For the formation of this metastable crystal, diffusion is only required within one unit cell, it is thus preferred when the diffusion of atoms is slow.

Spinodal decomposition can occur only when the total of the chemical free energy change ΔG_c , the interfacial energy ΔG_i , and the strain energy ΔG_s induced by spinodal decomposition is negative. The chemical free energy change ΔG_c is approximately equal

to ΔG_2 in Fig. 5-4. The interfacial energy ΔG_r can be related to the wavelength of spinodal decomposition λ and the composition difference $(C_2 - C_1)$ by

$$\Delta G_r = K[(C_2 - C_1)/\lambda]^2 \quad (5-2)$$

K is a proportionality constant. The strain energy can be expressed as

$$\Delta G_s = \eta^2 (C_2 - C_1)^2 [E/(1 - \nu)] V_m \quad (5-3)$$

η is the fractional change in lattice parameter per unit composition. E is the Young's Modulus, ν is the Poisson's ratio. V_m is the molar volume. Therefore,

$$\Delta G_2 + K[(C_2 - C_1)/\lambda]^2 + \eta^2 (C_2 - C_1)^2 [E/(1 - \nu)] V_m \leq 0 \quad (5-4)$$

The critical wavelength is

$$\begin{aligned} \lambda_{c-s} &\leq \sqrt{-[\Delta G_2 + \eta^2 (C_2 - C_1)^2 [E/(1 - \nu)] V_m] / [K(C_2 - C_1)^2]} \\ \lambda_{c-s} &\leq \sqrt{-(\Delta G_2 / [K(C_2 - C_1)^2] + \eta^2 [E/(1 - \nu)] V_m)} \end{aligned} \quad (5-5)$$

λ_{c-s} is less than 10 nm at the annealing temperature, since the wavelength of the nanolamellar structure is less than 10 nm.

(b) Formation of eutectic phases. From eutectic solidification theory, the minimum possible spacing for the eutectic phases (eutectic lamellar) λ_{c-e} can be expressed as

$$\lambda_{c-e} = -2\gamma_e / \Delta G_{v-e} \quad (5-6)$$

γ_e is the interfacial energy of eutectic phases (in our case, Co_2Si and Co_2B). ΔG_{v-e} is the volume free energy change from metallic glass to eutectic phases, it is equal to the sum of ΔG_1 , ΔG_2 and ΔG_3 in Fig. 5-3. Assuming γ_{M-G} is close to γ_e , and comparing equation (5-1) and (5-6), to get a λ_{c-e} less than 10 nm, implies that the ratio of ΔG_{v-e} to ΔG_{v-M} is more than 10.

The nanolamellar structure itself has reasonable thermal stability; it can retain good periodicity for long annealing time after its formation implying that the interfacial energy ΔG_r should be small. This means that ΔG_2 from equation (5-5) can be small. Here a simple calculation is provided to estimate the wavelength of the eutectic lamellar

structure, based on the DSC result. The interfacial energy γ_{M-G} can be assumed to be 1 Jm^{-2} , which is close to the interfacial energy of disordered grain boundaries; r_c is assumed to be 100 nm, ΔG_{v-M} can thus be about $2 \times 10^7 \text{ Jm}^{-3}$. The melting point of Co-Si-B ternary alloys [229] with composition close to $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy is about 1100°C ; the annealing temperature is 500°C . Using the approximation $\Delta G_v = \frac{H_v \Delta T}{T_m}$, the heat involved during the crystallization of the metastable crystal can be calculated to be about $4 \times 10^7 \text{ Jm}^{-3}$. From the DSC result (Table 4-1), the heat involved in the first reaction of heating is 85 J/g ; the density of this amorphous alloy is $7.6 \times 10^6 \text{ gm}^{-3}$, it can be shown that the heat involved in the formation of metastable phase is about 2/3 of that during crystallization of the metastable phase with the nanolamellar structure. From the DSC result, the second peak is very small, thus the heat involved is small. Therefore, the heat of crystallization into the metastable phase is approximated as 1/2 of that of crystallization into eutectic phases. Again using the relationship $\Delta G_v = \frac{H_v \Delta T}{T_m}$ and equation (5-6), the minimum possible spacing for eutectic phases (eutectic lamellar) λ_{c-e} is about 50 nm. This value is close to that of the coarsened microstructure in Fig. 4-21.

From the above thermodynamic analysis, it is seen that formation of metastable phase and spinodal decomposition is preferred in the crystallization of the amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy. The spinodal decomposition may occur concurrently with metastable crystal formation since it only involved 8~9 layers of unit cells. That the nanolamellar structure is modulated in the (0 0 1) plane may be attributed to the larger interfacial energy for interfaces perpendicular to the (0 0 1) plane. This microstructure can be also modified by annealing conditions, e.g., using large heating rate and annealing at high temperature, the formation of the metastable crystal may be bypassed due to the high mobility of atoms, leading to the formation of the equilibrium phases.

5.1.5 Coarsening of nanolamellar structure and formation of equilibrium phases.

Table 5-1 Crystal parameters of the phases involved in the coarsening of nanolamellar structure. [230]

[illegible]

a), Co phase is expected to form. Co phase has a lattice parameter of 0.3545 nm, which is about half of (1 0 0) plane and (0 0 1) plane distance of the crystal with nanolamellar structure (Fig. 5-5 a); with effect of the alloying elements Si or B, the lattice parameter is increased. From Fig. 4-27 and Table 4-4, it can be seen that the Co phase was highly faulted. Co_2Si can also nucleate heterogeneously from the grain boundary (Fig. 5-5 b). The Co_2Si usually precipitated from the boundaries which are nearly parallel to the lamellae (Fig. 4-21 c&d). Nucleation of the more stable phases from the grain boundary is chemically preferred.

Fig. 5-5 Schematic of precipitates at grain boundaries.

The growth of precipitates at the grain boundaries induced a composition variation in the neighboring region. This composition variation facilitates the nucleation of the other stable phases. For example, when Co_2Si was precipitated, the neighboring region would be Si poor and B rich, Co_2B phase was thus nucleated; these Co_2Si and Co_2B phases have very low solubility of elements (from ternary phase diagram in Ref. [229]), some Co

phase can also form. Therefore, coarsening from the grain boundaries usually produced a coarse lamellar structure (Fig. 4-22). Coarsening from the grain boundary and formation of a coarse lamellar structure indicated that the diffusion and transfer of the atoms at the interface was much faster than from the lattice, indicating that continuous coarsening of the nanolamellar structure was negligible.

Precipitation from within the grains was also observed. This type of precipitates was rod shaped and parallel to the lamellae (Fig. 4-23). The density of these precipitates is much lower than grain boundary precipitates; they precipitated from lattice defects such as dislocations and stacking faults; a crack can greatly enhance the density of this type of precipitate (Fig. 4-23 a). In Fig. 4-23, it can also be seen that the thickness of these precipitates is about that of two layers of the lamellae. The coarsened precipitates from within the grains were determined to be Co_2B (Fig. 4-24), this phase has an interplanar distance of 0.5015 nm in (1 0 0) plane, which is close to that of half of the (0 1 0) planar distance of the nanolamellar phase. It can thus form a semi-coherent interface [2 2 4] with the matrix grain. Fig. 5-6 schematically illustrated the formation of such a precipitate.

Fig. 5-6 Precipitation within the grain. (a) a schematic dislocation and (b) Co_2B formation is preferred.

It is interesting to observe that another metastable phase Co_3Si phase formed during the coarsening of the nanolamellar structure (Fig. 4-24, Fig. 4-25 and Fig. 4-26). From Fig. 4-24, the orientation relationship of Co_2B phase and Co_3Si phase was determined to

-----Discussion: Crystallization behavior of cobalt based alloy-----

be $(1\ -1\ 0)_{\text{Co}_2\text{B}} // (2\ 0\ 0)_{\text{Co}_3\text{Si}}$ and $(1\ 1\ 2)_{\text{Co}_2\text{B}} // (0\ 0\ 2)_{\text{Co}_3\text{Si}}$; from Fig. 4-25, the orientation relationship of Co and Co_3Si was determined to be $(0\ 2\ 0)_{\text{Co}} // (0\ 0\ 2)_{\text{Co}_3\text{Si}}$ and $(2\ 0\ 2)_{\text{Co}} // (2\ 0\ 0)_{\text{Co}_3\text{Si}}$. The orientation relationships between Co_2B phase, Co phase and the grain with nanolamellar structure is schematically illustrated in Fig. 5-5 (b) and Fig. 5-6 respectively. Thus it is expected that the $(2\ 0\ 0)$ plane of Co_3Si has a 45° angle with the $(0\ 2\ 0)$ plane of grain with nanolamellar structure; the $(0\ 0\ 2)$ plane of Co_3Si is perpendicular or parallel to the $(2\ 0\ 0)$ or $(0\ 0\ 2)$ plane. A schematic of the mechanism of phase transformation from grain with nanolamellar structure to Co_3Si phase is illustrated in Fig. 5-7.

Fig. 5-7 Formation of metastable Co_3Si phase from the nanolamellar crystal. (a) Possible crystallographic orientation relationship and (b) projection from $[001]$ direction. (c) and (d) shows the crystallographic orientation relationship of Co_3Si with Co_2B and Co respectively. The dashed lines indicate the Co_3Si crystal.

This metastable Co_3Si phase was subsequently consumed by the equilibrium Co_2Si , Co_2B and Co phases. Therefore, the strong peak at around 43° present in the XRD results of samples heat treated at 560°C for 60 min and 120 min disappeared in the XRD data of samples heat treated for 240 min and 900 min (Fig. 4-7).

Due to higher interfacial energy, the coarse lamellar structure such as in Fig. 4-22 and in Fig. 4-24 was not stable for long time or high temperature heat treatment. It broke up into equiaxed grains (Fig. 4-13 and Fig. 4-14). A careful composition analysis by EDX was carried out on the equiaxed grains (Fig. 4-28 and Table 4-5). The composition analysis was consistent with that the equiaxed grains were formed from the coarse lamellae (Fig. 4-28 a). In Table 4-5, the three types of compositions are clearly distinguished. Co lean and Si rich phase was confirmed to be Co_2Si phase from SADP (Fig. 4-28 b). The faulted phase which has Co composition around 80 % was interpreted to be the Co phase (Fig. 4-28 c). The Co rich and very lean silicon phase was a boride phase with very little solubility of silicon atoms; this phase was the Co_2B phase.

With increasing heat treatment time, the equiaxed grains grew larger in size to reduce the interfacial energy, which led to the interconnection of grains belonging to the same phase. This interconnection could greatly increase the electron conductivity, in conformity with the resistivity results. Among Co_2Si , Co_2B and Co phases, only the Co phase is a good electric conductor; the initial grains with nanolamellar structure and Co_3Si phase also have a large electrical resistivity, the Co phase was thus the main path for electrons. However, when the Co phase was isolated by the Co_2Si and Co_2B phases, the conduction through Co phase was not activated; the resistivity of the sample was high (Fig. 4-2). The third large drop of resistivity during dynamic heating was thus due to the interconnection of cobalt grains; this occurred at around 750 °C under dynamic heating.

From the above analysis, the coarsening of the nanolamellar structure can be summarized in the following flow chart (Fig. 5-8).

Coarsening is a common phenomenon of fine microstructures due to their large interfacial energy [224, 232]. The coarsening of fine microstructures can be continuous as well as discontinuous. In modulated lamellar structure formed by spinodal decomposition, continuous coarsening by increasing the lamellar spacing was observed in heat treated natural alkali feldspars [233]. The coarsening of eutectic lamellar structure is reviewed in

Fig. 5-8 Coarsening process of the nanolamellar structure.

Ref. [232], the coarsening of the eutectic microstructure was initiated by defects such as grain boundaries and faults in alignment, supporting the coarsening theory of diffusion limited fault migration. In this nanolamellar structure formed by crystallization of the amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy, coarsening was initiated by precipitation at grain boundaries and from within the grains, which is a discontinuous coarsening process. Therefore to form a thermal stable nanolamellar structure, large grain size was required.

5.1.6 Correlation of microstructure and magnetic properties in the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy

The magnetic properties of materials depend on their composition, magnetic phases and microstructure [6]. Amorphous magnetic materials, which do not possess crystallographic anisotropy, show good soft magnetic properties with extremely low coercivity and large permeability. In Fig. 4-29, it can be seen that the melt spun $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ amorphous alloy has a very narrow magnetic hysteresis loop. Crystallization of this alloy resulted in a deterioration of the soft magnetic properties, leading to a large coercivity and reduced magnetization (Fig. 4-29 and Table 4-6). However interestingly, heat treatment at 480 °C for a time less than 3 h resulted in an

improvement in soft magnetic properties. A small decrease in coercivity and increase in magnetization was observed compared to the as-spun amorphous alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ in such samples. This is consistent with Yang [193] and Tsai [197]'s investigation.

In the first step of crystallization, the precipitation of a small amount of large grains from the initial amorphous alloy in sample heat treated at 500 °C for 10 min did not affect the initial magnetization process much. It can be seen that the squareness of the hysteresis loop was comparable with that of the as-spun ribbon. The coercivity was also much smaller than those of fully crystallized samples.

For fully crystallized samples, the coercivity initially increased to a maximum and then decreased (see section 5.1.2, Fig. 5-2). From Table. 4-6, it can be seen that the coercivity of the samples heat treated at 480 °C for 240 min is smaller than those of samples heat treated at 530 °C for 5 min although in both samples large grains with nanolamellar structure were the dominant microstructure. The difference can be attributed to two reasons: the grain size is larger and precipitates (at the grain boundaries and within the grains) are less in the sample crystallized at 480 °C. In conventional single phase coarse grained material, the coercivity is inversely proportional to the grain size. Precipitates also play an important role in the increase of coercivity. It can be seen that in samples heat treated at 530 °C for 30 min and 560 °C for 10 min, which had a large volume fraction of fine precipitates, the coercivity increased considerably due to the pinning of domain walls by precipitates. The heterogeneous microstructure which consisted of the coarse lamellae, should have a large coercivity due to the shape effect of coarse lamellae and the large strain in the heterogeneous microstructure. Therefore the coercivity increased to a maximum with the consumption of the initial large grains by the heterogeneous microstructure. The break-up of the coarse lamellae into equiaxed grains reduced the shape effect and thus decreased the coercivity. At this time, the grain size of the equiaxed grains is around 100 nm (Fig. 4-13 a). The increase in grain size (Fig. 4-13 b) decreased the coercivity to less than 1/3 of the maximum value.

The saturation magnetization (M_s) of materials is the weighted average of M_s of the phases present; it is relatively structure insensitive. The M_s remained at about 0.48 T in the crystallized samples of the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy. Differences in the M_s were due to the volume fraction of the magnetic phases developed in the sample.

From the above analysis, it can be seen that the nanolamellar structured grains had a M_s of around 0.48 T, no unusual magnetic behavior was observed due to the formation of nanolamellar structure.

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

In situ TEM is a state-of-art technique, which provides real time observation of microstructural evolution at elevated temperatures [234-237]. It can thus enable a better understanding of mechanisms as well as the modeling of relevant processes. In order to understand the mechanisms of nanolamellar structure formation, in situ TEM observation of the crystallization process of the amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy was carried out. However, due to the thickness effect, in situ thin foil crystallization yielded completely different crystallization products compared to conventional heat treatments.

Crystallization is a nucleation and growth process. The thickness dependence of crystallization is very obvious, the nucleation rate decreased with the increasing of foil thickness from Fig. 4-30. In the thin regions, spheroidal nanocrystals can form with a high nucleation density at a short time; in the medium thick regions faceted/elongated crystals formed; and in the thick regions, sparse crystals with irregular shapes formed. In the later stage, heterogeneous nucleation and growth dominate the crystallization of the remaining amorphous matrix in the thick regions, because no new nucleation event was detected although some of the precipitates changed their size or contrast after holding for

density. In the thin area of about 80 nm in thickness, an average precipitate size of about 16 nm is obtained; in the thick area of about 320 nm in thickness, the size of the precipitate cluster can reach 185 nm.

The precipitates possess a h.c.p Co phase in the thin area; in the thick area, besides h.c.p. Co phase, f.c.c Co phase was also formed (Fig. 4-33). Fig. 4-33 (b) showed weak diffraction spots besides the ring patterns corresponding to h.c.p phase. These diffraction spots belonged to the f.c.c Co phase, suggesting that some f.c.c Co phase was formed during the cooling process. The irregular shaped precipitates in the thick area consisted of several grains which are either h.c.p Co or f.c.c Co. The cluster of crystals has a crystallographic orientation relationship, e.g., in Fig. 4-33 (e), the (1 0 0) plane of f.c.c Co grains and (1 1 1) plane of h.c.p Co grains are parallel.

The different crystallization behavior of in situ crystallization and conventional crystallization was due to strain, thin foil diffusion and surface effects. The surface crystallization is nearly independent on the thickness of foil. Therefore, the thickness dependence of grain size is mainly due to strain and thin foil diffusion. The strain effect in the thin foil is like a negative pressure effect [163-164], the magnitude should exhibit a (1/t) dependence. The free energy change during crystallization can thus be expressed as

$$\Delta G = V \cdot \Delta G_{v,a \rightarrow c} + S \cdot \gamma_{a-c} + \frac{\delta}{t} \cdot V. \quad (5-7)$$

Where V is volume of crystalline phase, $\Delta G_{v,a \rightarrow c}$ is the volume free energy change from amorphous to crystalline, γ_{a-c} amorphous-crystalline interfacial energy. δ is a constant which reflects the thickness dependence of negative pressure, Fig. 5-9 illustrates the relationship. When there is a Δt shrinkage of lattice, it will produce a negative pressure of $E \cdot \Delta t / t$, E is the Young's modulus. In the thin foil, when a crystal formed, it will produce a shrinkage of $\Delta V_{a \rightarrow c}$, this shrinkage is mainly in the thickness direction. In order not to confuse with Young's modulus E, the symbol δ is used. Therefore, from equation (5-7), the critical size for nucleation of spherical crystals is

Fig.5-9 Thickness dependence of strain energy.

$$d^* = \frac{3\gamma_{a-c}}{\Delta G_{v,a \rightarrow c} + \frac{\delta}{t}} \quad (5-8)$$

Equation 5-8 indicated that in the thin area, the critical nucleus size is smaller than in the thick area. From equation 5-8, it can also be seen that with increasing thickness, its effect on reduction of critical nucleus size decrease. This is consistent with the experimental observations that the crystal size remained at around 40 nm in the thick area although the precipitate (crystal cluster) size increased to more than 100 nm.

According to the theory of crystallization kinetics, the nucleation rate can be expressed as [164, 224]

$$I = I_0 \exp\left(-\frac{\Delta G^* + Q_n}{kT}\right) \quad (5-9)$$

ΔG^* is the thermodynamic potential barrier of nucleation, Q_n is the activation energy for transport of an atom across the interface of an embryo, k is the Boltzmann's constant. ΔG^* will be significantly decreased when the critical nucleus size is decreased. This suggests that the nucleation rate in the thin area will be much larger than in the thick area. If there is no composition difference between crystalline phase and amorphous phase, Q_n will also be decreased after precipitation because negative pressure enhances the mobility of atoms. This implies that the number of crystals will increase significantly with longer holding time and this effect will decrease with increasing thickness. This is also consistent with the experimental observations.

In the thick area, the nucleation rate is low, heterogeneous nucleation was preferred. It can be seen that the crystals in the thick area are faulted. In Kim [190] and Byeon [206] 's investigations, faulted f.c.c or h.c.p Co was formed in amorphous $\text{Co}_{95-x}\text{Fe}_5(\text{BSi})_x$ alloy, this phase was considered to be induced by oxidation. However, the thickness dependence morphology in the in situ crystallization of this alloy indicated that the oxidation may not play a significant role in the formation of these faults. The faults in the crystals are mainly induced by stress and solid solutes because of low atomic mobility.

During conventional heat treatment, heat treatment at around 400 °C for 3 h is not sufficient to crystallize this alloy. During in situ characterization, crystallization was not observed in the very thick area, which is consistent with conventional annealing. The occurrence of crystallization in the thin region at 400 °C again suggested that the mobility of atoms was increased in the thin area. The nanolamellar structure did not form during thin foil crystallization because (a) the crystal with nanolamellar structure was metastable and (b) the mobility of atoms was increased in the thin foil. The equilibrium Co_2Si and Co_2B phases were not formed during in situ crystallization because the solid solubility in these crystals is small and formation of these two phases needs a long range of diffusion.

5.1.8 In situ TEM observation of the coarsening process of nanolamellar structure

From in-situ TEM observations (Fig. 4-34), the overall coarsening process of nanolamellar structure can be described in three steps: (a) precipitation of fine precipitates, (b) distortion of nanolamellae, and (c) formation of a multi-phases structure. The steps (a)

fine precipitates, it suggested that this precipitation is purely a surface effect, which could be due to surface oxidation or special atomic structures at the surface. In Byeon's work [206], oxide precipitates were formed in crystallized substrate of $\text{Co}_{74.26}\text{Fe}_{4.74}\text{Si}_{2.1}\text{N}_{18.9}$ after annealing at 250 °C in the air. The oxide precipitates in their work were in amorphous state and interpreted to be borosilicates. In our work, in-situ TEM was carried out in ultra high vacuum conditions, ruling out serious oxidation; however, due to the trapping of oxygen atoms in the sample, release of oxygen at elevated temperature can occur and surface oxidation can take place. Although these fine precipitates did not greatly affect the nanolamellar structure, they served as heterogeneous nucleation sites for precipitation in the third step. The large precipitates in Fig. 4-35 (d) were not the result of growth from the fine spherical precipitates but were instead the discontinuously coarsened product of the nanolamellar structure.

The coarsening of nanolamellar structure began by corrugation of the lamellae and

structure. It can also be seen that this type of coarsening depends on the orientation relationship of nanolamellae with the boundary and lamellae in neighboring grains [238]. As indicated in Fig. 4-36 (b), very little change in grain boundary *I* occurred although in boundary *II* and *III* large changes had taken place. Boundary *I* is nearly parallel to the lamellae while boundary *II* and *III* have a high angle with the boundary as well as the neighboring lamellae in boundary *II* and *II*. This difference can be attributed to the atomic configurations and compositions at the grain boundaries.

The third step is a multi-phase formation process. As the equilibrium phases from Co-Si-B ternary phase diagram [229] are Co_2Si , Co_2B and h.c.p. Co for a composition close to the alloy composition used in this investigation, transformation to these phases takes place. The mobility of atoms at surfaces and grain boundaries is usually higher than within the bulk crystal. Therefore, this step was initiated from the surface by heterogeneous nucleation at the fine spherical precipitates formed in the first step as well as from the grain boundaries. As shown in Fig. 4-37, large precipitates (black in contrast) were observed and their size increased with increasing of holding time; new precipitates (white in contrast) continued to emerge near the grain boundaries; further nucleation and growth of precipitates as well as dissolution of some precipitates were also observed; finally the multiphase structure was formed. A similar precipitation process was also observed in other grains. It thus can be concluded that the precipitate formed earlier is metastable; the precipitates which formed later caused the dissolution of these earlier formed precipitates and they consumed some of the matrix phase; equilibrium composition was then reached and a mixture of phases formed. These two types of precipitates are the Co_2Si and Co_2B phases. In Fig. 4-37 (c) and (d), some faulted precipitates were observed, which may belong to the Co phase.

The time periods for these three steps are not clearly separated and can overlap to some extent. For example, discontinuous coarsening from the grain boundaries actually involved the formation of the multiphase mixture (third step), however it occurred at

almost the same time as the corrugation of nanolamellae (second step). Comparison of these processes can provide information on the effect of grain boundaries, lamellar interfaces and the surfaces on the coarsening of nanolamellae. This will be discussed in detail later.

The difference in the coarsening process of in-situ and conventional annealing is due to surface effects. In in-situ annealing, a thin foil sample was used, in which a large portion of atoms is at or near the surface, the surface effects thus play a significant role in coarsening.

In the conventionally annealed sample, it can be observed that the nanolamellar structure retains good periodicity although a large portion of the grain was consumed by the discontinuously coarsened microstructure (Fig. 4-22). This discontinuous coarsening was initiated at the grain boundary. This is different from the in-situ coarsening process in which the nanolamellar structure became corrugated along with the discontinuous coarsening (Fig. 4-36). The final microstructure from conventional annealing (Fig. 4-13) consisted of near-spherical grains similar to the final product of in-situ annealing. The phases were interpreted to be a mixture of Co_2Si , Co_2B , h.c.p. & f.c.c. Co and Co_4B (section 5.1.1).

It can thus be concluded that the surface plays a significant role in coarsening while it does not affect the identity of the final product. The surface effects led to a continuous coarsening of the nanolamellar structure and formation of a metastable phase which has a similar crystal structure to the original nanolamellar structured crystal. Discontinuous coarsening from the grain boundaries was also affected by surface effects. In conventional annealing, discontinuous coarsening led to a coarse lamellar structure which consisted of several phases; due to the large interfacial energy between the lamellae they were metastable and broke up into near spherical grains. In the case of the in-situ annealing, discontinuous coarsening started by the nucleation of one phase at either grain

boundaries or at the surface; this was followed by heterogeneous nucleation of a new phase from the earlier phase, resulting in a multiphase microstructure.

Microstructures try to reach a minimum energy but are kinetically controlled by diffusion [224]. The coarsening process occurred mainly because of the large interfacial energies. The instability of the nanolamellar structure in this investigation can be attributed to the energy of the metastable crystal structure, composition of the lamellar structure and the interfacial energy between the nanolamellae. To reduce the interfacial energy between the nanolamellae, continuous coarsening by reducing the number of nanolamellae is preferred; while to reduce the energy of the metastable crystal, discontinuous coarsening by the formation of new stable phases is preferred.

To determine which coarsening process will dominate we need to compare the driving force of continuous coarsening and discontinuous coarsening. For this highly modulated nanolamellar structure, a coherent interface is assumed. Thus the interfacial energy of nanolamellae occurred mainly due to change in bonding environment of the atoms in the interface. γ_{ch-A} is used to represent this type of interfacial energy. At the grain boundaries, the interfacial energy will include contributions due to the changes in bonding of atoms at two neighboring grains γ_{ch-B} , the strain energy γ_{ch-C} and also the interfacial energy of nanolamellae γ_{ch-A} . At the surface, the energy making the structure unstable includes contributions from atoms in the surface layer γ_{ch-D} and γ_{ch-A} . The driving force per unit area for the coarsening of a small volume selected from interlamellae, different grain boundaries and surface (as schematically illustrated in Fig. 5-10) can be represented as

(a) Interlamellae.	$F_I = \gamma_{ch-A}$
(b) Boundary I.	$F_{B-I} = 2\gamma_{ch-A} + 2\gamma_{ch-B} + 2\gamma_{ch-C}$
(c) Boundary II	$F_{B-II} = (>4)\gamma_{ch-A} + (>2)\gamma_{ch-B} + (>2)\gamma_{ch-C}$
(d) Surface	$F_S = 2\gamma_{ch-A} + \gamma_{ch-D}$

Fig. 5-10 Schematic interfacial conditions with nanolamellar structure. (a) Interlamellae, (b) grain boundary oriented parallel to the nanolamellae of one neighboring grain (Grain boundary I), (c) grain boundary having a large angle to the nanolamellae, (d) free surface with nanolamellae perpendicular to the surface.

The number used before the γ in the above equations represents how many such interfaces

5.2 Mechanical alloying processing of cobalt based amorphous magnetic alloys

Mechanical alloying is a low-cost and versatile technique in processing amorphous and nanostructured materials. Amorphous cobalt based magnetic alloys, which showed superior soft magnetic properties, were successfully prepared through MA starting from elemental powders. The alloying and amorphous phase formation by mechanical milling method is discussed. The as milled amorphous alloy powders had soft magnetic properties comparable to the melt spun amorphous alloys but annealing of these powders caused a deterioration of the soft magnetic properties. A comparison of MA amorphous alloys with melt-spun amorphous alloys is included in this section.

5.2.1 Alloying process and amorphization

Alloying by mechanical milling can be attributed to be the repeated fracturing, welding and diffusion during milling of powders [25, 81]. For the milling of ductile and brittle materials, the brittle powders broke up into smaller size powders and were trapped in the ductile powders; alloying was induced by short range diffusion after more energy and heat was introduced into the powders through milling.

For the milling of powders with composition $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$, Co, Fe and Ni elemental powders behaved as ductile material and occluded the fragmented metalloid Si and B powders in the initial stage of milling (Fig. 4-38 a). In Fig. 4-38 (a), fine powders

The alloying process of $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ was similar to that of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$. With ductile Co powders enclosing the brittle fragments of elemental powder Si and B (Fig. 4-39 a & b), alloying occurred at the interface of the brittle fragments and ductile Co particles; with further milling and fracturing of the particles (Fig. 4-39 c & d), alloying and homogenization of composition was realized. An obvious increase of particle size was observed in 150 min milled $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ powders (Fig. 4-39 b), suggesting a welding dominated milling process.

The XRD and DSC results indicated amorphous phase formation after milling. As shown in Fig. 4-40 and Fig. 4-41 for the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ alloys respectively, below the broad peak (corresponding to the Co phase), a large hump can be observed in the 5 h as milled powders, suggesting the formation of the amorphous phase. The broad peak suggested that the Co phase was highly faulted at this stage. Amorphization continued under further milling: only broad humps were observed in the XRD results of the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ powders milled for 10 h and longer time (Fig. 4-40); for $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ powders, the intensity of the broad h.c.p. Co peak decreased with longer milling time and only a broad hump was detected for powders milled for 40 h (Fig. 4-41). The difference in behavior during dynamic heating of powders milled for 150 min and those milled for 20 h, 40 h, 80 h (Fig. 4-42 and Fig. 4-43) also suggested the formation of an amorphous phase: a large exothermic hump for 150 min milled powders corresponded to stress relaxation; the exothermic peaks observed in 20 h, 40 h and 80 h milled powders corresponded to the crystallization of amorphous phase. The exothermic peak at around 700 °C in the DSC curve of 150 min milled powders (Fig. 4-42 and Fig. 4-43) suggested a crystallization process. The DSC results also showed that crystallization temperatures of the as milled powders decreased with an increase in milling time. This can be due to the following reasons: (a) the amorphous phase has a higher crystallization temperature, after homogenization of the composition, the crystallization temperature decreased; (b) crystallization of the amorphous phase was induced during milling and the crystallized

phase acted as a nucleation site for crystallization during heating; (c) more stress induced for longer milling time aided crystallization during heating; and (d) contamination by the milling media introduced Fe, C and Cr etc. into the powders, which decreased the crystallization temperature of the amorphous phase formed.

The above analysis of alloying process and amorphous phase formation suggested that alloying and amorphous phase formation occurred simultaneously. Firstly, from the DSC results of 150 min milled powders, besides the stress relaxation humps, an exothermic crystallization peak was observed at around 700 °C (Fig. 4-42 and Fig. 4-23). At this stage of milling, alloying just started from the morphological observations of the powders (Fig. 4-38 b and Fig. 4-39 b). The XRD results of 5 h milled powders, which showed broad h.c.p. Co peaks, indicated that some Co did not react after 5 h of milling; i.e., a large volume fraction of elemental Co had not alloyed after 150 min of milling. Secondly, amorphization was fast, especially for powders with nominal composition $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$: after only 5 h of milling, a large volume fraction of amorphous phase was formed (Fig. 4-40 a and Fig. 4-41 a); after 10 h of milling, only the amorphous phase was detected using XRD (Fig. 4-40 b); 20 h milled powders showed sharp exothermic peaks during dynamic heating (Fig. 4-42 and Fig. 4-43). This process is even faster than amorphization from crystallized amorphous ribbons with similar composition. In Kaczmarek's work [110] 50 h of milling was required to complete the reamorphization of $\text{Co}_{70.3}\text{Si}_{15}\text{B}_{10}\text{Fe}_{4.7}$ crystalline alloy and in Matyja's work [213] more than 50 h was used to reamorphize the $\text{Co}_{66}\text{Fe}_{12}\text{Si}_9\text{B}_{13}$ alloy. Therefore, amorphization was not a subsequent reaction after formation of the crystalline phase from elemental powders; instead it was a direct process from elemental powders. The amorphous phase was expected to be boron rich since the exothermic crystallization peak and hump of 150 min milled powders (Fig. 4-42 and Fig 4-43) appeared at high temperatures and the temperature for crystallization into boride phase is usually high [161, 239]. The center of the hump in the XRD results (Fig. 4-40) was at a higher value of 2θ for 5 h milled powders than for longer time milled

powders, suggesting that the near neighbor atoms had a smaller distance, the amorphous phase was thus possibly boron rich. This can be attributed to two reasons: boron itself aids in amorphization and boron can diffuse readily. Boron is also an important element for the amorphization of Fe-Si-B alloys [97, 100, 151].

The alloying process and formation of amorphous phases is summarized in Fig. 5-11.

Fig. 5-11 Block diagram of alloying and formation of amorphous phase during milling.

5.2.2 Magnetic properties of as milled and annealed powders

Importantly, mechanical milling (MM) yielded powders exhibiting soft magnetic properties (Fig. 4-44 and Fig. 4-45). The coercivity of some powders was small and about 800 A/m, which is comparable with pure Fe powders (910 A/m measured using the same equipment). MM can thus be used to produce soft magnetic materials [21].

From Fig. 4-44 and Fig. 4-45, it can be seen that the saturation magnetization decreased continuously with milling time in the as milled powders, indicating a continuous phase transformation process. The saturation magnetization of a material is a simple weight ratio sum of the magnetic phases it contained. For the composition $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$, the starting powder mixture was calculated to have an M_s of 1.26 T;

this value was close to the M_s of 50 min as milled powders (Fig. 4-44). The M_s of powders with both composition exhibited three steps of variation during milling: slowly decreased (100 min and 150 min), dramatically decrease; stabilization (longer than 32 h).

The coercivity of the starting powder mixture was determined by the H_c of h.c.p. Co (since it is the magnetically hardest phase in the mixture) and was about 13530 A/m,

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decrease of M_s and increase of H_c . In 20 h milled $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ powders both M_s and

~~*LL decreased asymptotic stress relaxation because of smaller initial strain rate.*~~

powders. Fe and Ni thus increased the crystallization temperatures of the amorphous phase and facilitated the mechanical crystallization process.

5.2.4 Comparison of MA amorphous and melt-spun amorphous phase

The amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy prepared by MA can be compared with melt-spun amorphous alloy: firstly, the XRD results for amorphous phase prepared by these two techniques were similar, both showed a broad hump in the range of 40~50 degree; secondly, the crystallization event of amorphous phase prepared by 20 h MA occurred at a temperature close to that of melt-spun alloy; thirdly although the soft magnetic properties was inferior in MA amorphous alloys compared to the melt spun ones, the M_s of 20 h milled powders after 400 °C annealing is close to that of melt spun amorphous alloy. The larger coercivity in MA amorphous alloys was mainly due to crystallization induced by MM and morphology of MA powders. As overheating [25] and heterogeneous nucleation [110] were the reason of crystallization, it would be better if low energy MM after amorphization was selected to homogenize the composition and a surface active surfactant was used to avoid sticking of the powders. Due to the fine particle morphology and small holes inside each particle, the domain wall was pinned and large coercivity was observed in MA powders. From the DSC results, it appeared that the stresses did not play an important role in the large coercivity of MA amorphous powders. The stresses could be relaxed for lower temperature annealing before crystallization, e.g. in the 20 h milled powders, a decrease of H_c was observed after 400 °C annealing for 2 h. The H_c in MA amorphous powders was comparable to the Fe powder and much smaller than the Ni bulk sample, suggesting the prepared powders were magnetically soft.

Kollár [215] compacted 4 h milled amorphous powders from crystallized $\text{Co}_{70.3}\text{Fe}_{4.7}\text{Si}_{10}\text{B}_{15}$ melt-spun ribbons and obtained bulk metallic glass with good soft magnetic properties. Bulk metallic glass could be also possibly prepared by compaction of properly mechanical alloyed amorphous alloy powders since compaction of the as milled powders may be able to reduce H_c .

5.3 Nanocrystallization behavior of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous magnetic alloy

HiTperm (Co-Fe-Zr-B-Cu) is one family of soft nanocrystalline magnetic alloys. In this investigation, $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous magnetic alloy in which Cu was not added was studied, a nanocrystallization behavior was observed. Unlike the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ amorphous magnetic alloy, this $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous magnetic alloy crystallized into a thermally stable microstructure of high density nanocrystals (less than 30 nm) in an amorphous matrix. The nanocrystallization process, microstructural characteristics, relationship between microstructure and magnetic properties of the $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy are discussed in this section. A comparison of this Cu free $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy with Cu containing HiTperm alloys is also included.

5.3.1 Primary crystallization behavior of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous magnetic alloy

DSC and electrical resistivity measurements were used to study the crystallization behavior of amorphous materials. From the DSC curves (Fig. 4-48) and dynamic electrical resistivity curve (Fig. 4-49), amorphous $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy displays a primary crystallization behavior since there are two sets of exothermal peaks and two sharp electrical resistivity drops at elevated temperatures. From Fig. 4-50, it is seen that the DSC curve and the derivative curve of electrical resistivity match well with each other, indicating that the electrical resistivity has a simple relationship with the primary crystallization of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ and can be used as a probe of crystallization.

The activation energies were determined using Kissinger analysis [222] to be 4.2 ± 0.1 eV/atom and 5.4 ± 0.2 eV/atom respectively for primary and secondary crystallization of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy (Fig. 5-12). Compared to the activation energy 3.35 eV/atom for primary crystallization of $\text{Co}_{44}\text{Fe}_{44}\text{Zr}_7\text{B}_4\text{Cu}_1$ alloy [180], the activation energy for the primary crystallization of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ was higher; Cu therefore seems to aid in the primary crystallization process.

Fig. 5-12 Kissinger plot for determination of activation energies of (a) primary crystallization and (b) secondary crystallization of amorphous $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy.

As reported by Ping [183], Cu did not form clusters or crystalline unlike in Finemet and Nanoperm alloys. However, compared to HiTperm alloy with copper addition [182], the exothermal peaks shifted to lower temperatures (about 5 °C lower) when the heating rate was 10 °C/min, this was explained by the idea that addition of Cu might decrease the melting point [183]. Since the activation energy was larger in Cu free $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ than in $\text{Co}_{44}\text{Fe}_{44}\text{Zr}_7\text{B}_4\text{Cu}_1$, the role of Cu may be to act as a favorable site for heterogeneous nucleation, e.g., by introducing local compositional changes [166].

The electrical resistivity variation with holding time at 450 °C, 465 °C and 485 °C (Fig. 4-51) showed a monotonic decrease with holding time during the primary crystallization event, again indicating a simple relationship between resistivity and crystallization. The rate of resistivity decrease with holding time increased with an increase in holding temperature, suggesting that the reaction rate of crystallization increased with increasing temperature. At the later stage of holding, the resistivity decreased very slowly with holding time due to the slow crystallization process of the remaining amorphous matrix. A detailed analysis of electrical resistivity data is included in section 5.3.2.

The XRD results indicated that α -(Co, Fe) formed during the primary crystallization event and the volume fraction of crystals increased significantly from 20 min to 120 min

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of holding at 450 °C (Fig. 4-52). High temperature of 600 °C for a long annealing time of 24 h led to serious oxidation of the ribbon surface. An oxide phase was detected in the XRD result of 600 °C for 24 h (Fig. 4-53).

5.3.2 Parameters calculation for primary crystallization of Co_{44.5}Fe_{44.5}Zr₇B₄ from electrical resistivity curves.

From Maxwell's treatment of a system composed of two materials of resistivities ρ_c and ρ_a in the form of

spheres of one resistivity in a medium of a different resistivity [241], the relationship between the electrical resistivity ρ_v and the volume fraction of precipitate χ_v can be expressed as

$$\rho_v = \frac{\rho_a [1 + \chi_v \Delta r]}{[1 - 2\chi_v \Delta r]} \tag{5-10}$$

Where Δr is given by

$$\Delta r = \frac{\rho_c - \rho_a}{2\rho_c + \rho_a} \tag{5-11}$$

ρ_c , ρ_a are the electrical resistivity of crystalline precipitate and amorphous matrix respectively. Thus.

-----Discussion: MA cobalt based amorphous magnetic alloy-----

are shown in Fig. 4-49, assuming a linear relationship of electrical resistivity and temperature. Thus when $300\text{ }^{\circ}\text{C} < T < 600\text{ }^{\circ}\text{C}$, the electrical resistivity of amorphous $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ can be expressed as (equation 4-1)

$$\rho_a(T) = 2.64 \times 10^{-3} T + 1.005$$

For crystalline precipitates, in the temperature range $300\text{ }^{\circ}\text{C} < T < 600\text{ }^{\circ}\text{C}$, the electrical resistivity can be expressed as (equation 4-2)

$$\rho_c(T) = 9.58 \times 10^{-3} T + 0.099$$

Therefore, the electrical resistivity of amorphous phase and crystalline precipitates at three isothermal temperatures can be calculated, as follows

$$\rho_a(450^{\circ}\text{C}) = 1.124, \rho_c(450^{\circ}\text{C}) = 0.530$$

$$\rho_a(465^{\circ}\text{C}) = 1.128, \rho_c(465^{\circ}\text{C}) = 0.544$$

$$\rho_a(485^{\circ}\text{C}) = 1.133, \rho_c(485^{\circ}\text{C}) = 0.563$$

Δr at specific temperature can be also calculated,

$$\Delta r(450^{\circ}\text{C}) = -0.272$$

$$\Delta r(465^{\circ}\text{C}) = -0.263$$

$$\Delta r(485^{\circ}\text{C}) = -0.252$$

Using these values, the crystalline volume fraction of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ held at $450\text{ }^{\circ}\text{C}$, $465\text{ }^{\circ}\text{C}$ and $485\text{ }^{\circ}\text{C}$ could be calculated from the resistivity curves (in Fig. 5-13). From Fig. 5-13, it can be seen there are three steps in the slope of the crystalline volume fraction v/s $\ln t$ curves. These three steps may be dominated as the annealing time increases by atomic ordering of the amorphous structure, nucleation and grain growth, respectively.

The kinetics of isothermal crystallization can be described by the Johnson-Mehl-Avrami equation: [137, 148]

$$\chi_v(t) = 1 - \exp[-b(t - t_0)^n] \quad (5-15)$$

Where n is an exponent, b is a rate constant (which depends on both the nucleation rate and the growth rate), and t_0 is the incubation time. Rewriting Eq. (5-15),

Fig. 5-13 Crystalline volume fraction variation with time at 450 °C, 465 °C and 485 °C in $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy, as calculated from isothermal electrical resistivity data.

Fig. 5-14 JMA modeling of the crystallization characteristics using electrical resistivity data.

$$\ln\{-\ln[1 - \chi_v(t)]\} = \ln b + n \ln(t - t_0) \quad (5-16)$$

From equation (5-16), exponent n and growth rate b can be obtained by plotting $\ln\{-\ln[1 - \chi_v(t)]\}$ v/s $\ln(t - t_0)$ using the crystalline volume fraction data obtained from isothermal electrical resistivity analysis, as shown in Fig. 5-14. The incubation time used here is estimated as the isothermal time when atomic ordering of the amorphous structure dominates (Fig. 5-13), which was 110 s, 640 s and 2210 s respectively at the temperatures 485 °C, 465 °C and 450 °C. From the fitting line and equation in Fig. 5-14, the exponent n

and growth rate b were obtained. The average n at three temperatures 485°C, 465°C and 450°C is 0.85. The n value is larger when the isothermal temperature is lower. The relatively low n value might be produced because of the experimental uncertainties in determination of incubation time, i.e., the incubation time might be shorter than those calculated from the above method. A trial analysis, which supposed the incubation time to be 0 s, showed that n is about 1.5. As in Ref.[137], that n is 1.5 indicates a primary crystallization behavior.

5.3.3 Overall microstructural observations

TEM was useful to further investigate the crystallization behavior of amorphous $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy from microstructural observations. From TEM observations, it is interesting to note that the crystallization products were insensitive to the heat treatment temperatures in the range of 400 °C to 465 °C (Fig. 4-54 to Fig. 4-58). For all the heat treatment temperatures involved, a high density of nanocrystals formed after holding for sufficient long time. At 400 °C and 420 °C, the crystallization was slow; a large increase in number and size of nanocrystals was observed with increasing holding time (Fig. 4-54 and Fig. 4-55). At both temperatures, a low density of nanocrystals was crystallized for holding time less than 240 min. Initially the nanocrystals had a relatively regular shape and appear to be single crystals with a size of about 10 nm (Fig. 4-55 a & b); after holding for longer time 400 °C and 420 °C, they appeared to be irregular clusters and grew to larger size (Fig. 4-55 c & d). The irregular shaped crystals were also observed in HiTperm alloy with copper additions and some Nanoperm alloys without copper addition [183]; they were suspected to be clusters of nanograins which were closely oriented. From our investigation, these crystals were instead shown to be single grain crystals (see detailed microstructural analysis in section 5.3.4). For 450 °C, 465 °C and 600 °C heat treatment temperatures, the crystallization occurred rapidly; after only a few minutes holding at these temperatures, a high density of nanocrystals were formed (Fig. 4-56, Fig. 4-57 and Fig. 4-58). The morphology of nanocrystals are the same as those obtained after

low temperature and long time heat treatment; their overall irregular shape did not change much for longer time of holding at 450 °C and 465 °C; the size can reach 60 nm.

Using EELS and XEDS techniques [218], the thin foil thickness was estimated. The nucleation density and crystalline volume fraction were then calculated using these thickness values (Fig. 4-63). From Fig. 4-63 (a), the nucleation density can be as high as $2 \times 10^{22} m^{-3}$ for samples annealed at 450 °C, and samples annealed at 400 °C and 420 °C for 240 min. For relatively short annealing time at 400 °C and 420 °C, nucleation densities are lower (lower than $5 \times 10^{21} m^{-3}$). Only a few nuclei were observed for samples annealed at 400 °C for 20 min and 60 min, and samples annealed at 420 °C for 20 min. It is thus concluded that nucleation in amorphous $Co_{44.5}Fe_{44.5}Zr_7B_4$ did not follow a constant rate mode, unlike in METGLAS 2826A [148] and some Ni-Ti-B glassy alloys [145]. It has also been suggested that if the nucleation stops in a short time, it will correspond to a fixed number of nucleation sites (quench-in nuclei) [145]. Although the nucleation densities showed little increase for samples annealed at 450 °C for 20 min, 60 min and 120 min, the hypothesis of “quench-in nuclei” could not be confirmed for the difficulty in quantitative analysis when the crystalline images overlap in TEM micrographs.

The crystalline volume fraction in Fig. 4-63 (b) showed a linear increase with time after annealing at 450 °C, at this temperature the crystalline volume fraction reached 15 %; however this linear relationship did not occur in samples annealed at 400 °C and 420 °C, where the crystalline volume fraction remained below 15 % for the annealing times investigated. This was consistent with the crystalline volume fraction evolution calculated from electrical resistivity data (Fig. 5-11). In Fig. 5-11, three steps of crystalline volume fraction were observed. In the first step, the crystalline volume fraction was below 15 %; in the second step, the crystalline volume fraction was in the range 15 % ~ 45 %. The crystalline volume fraction obtained from TEM observation was a little higher compared with that calculated from electrical resistivity data.

Heat treatment at 600 °C and 700 °C induced secondary crystallization. For short time heat treatments at these temperatures, the microstructures were similar to those observed after lower temperature heat treatments. However, the irregular nanocrystals appeared more compact with an increase in holding time, this irregular shape was retained after 8 h of heat treatment; after holding at 600 °C for 24 h, the irregular crystals developed into relatively regular shape with a large size of about 40 nm (Fig. 4-58 d) and the SADP indicated that a secondary phase had formed. The sample heat treated at 700 °C for 4 h had a coarse equiaxed microstructure with grain size of about 150 nm (Fig. 4-59 a). Inside these large grains, many fine precipitates were observed. SADP analysis revealed that the $(\text{Fe, Co})_3\text{Zr}$ secondary phase had formed (Fig. 4-59 c). The dark field micrograph (Fig. 4-59 b) showed that the secondary phase was the precipitates within the large grains; the secondary phase had also formed at grain boundaries and tri-junctions.

5.3.4 Nanocrystallization, growth of nanocrystals and stability

In order to check if the “cluster” was a single crystal, conventional TEM observations, HRTEM and CBED techniques were used to study the heat treated samples. For these observations, many crystals in each sample were checked; typical results are shown in Fig. 4-64 and Fig. 4-65. In the early stage of crystallization (Fig. 4-64 a), the crystals have a relatively regular shape and the corresponding HRTEM micrograph indicates that this is a single crystal. At a later stage (Fig. 4-64 b), when the crystalline density was higher and the crystals was larger, the shape of crystals became irregular and a difference in contrast within the crystals was observed. When the crystalline density was much higher, the crystal had a dimension of more than 20 nm (Fig. 4-64 c) and looked like a cauliflower. However, in these later two stages, the corresponding HRTEM micrograph showed lattice fringes in the same direction, suggesting that the crystals were single crystals. Further evidence is provided: the CBED shows only one set of diffraction pattern from a crystal “cluster” (Fig. 4-65 a). The CBED was interpreted to be b.c.c. (Co, Fe) with the zone axis $[1\ 0\ 0]$. Fig. 4-65 (b) showed another crystal, the corresponding single crystal CBED and

HRTEM. Therefore, “clusters” are, in fact, single crystals, with the crystalline growth following a dendritic mode. The difference of contrast within the crystal is due to the thickness difference in the parts of the crystal relative to the thin foil.

The crystalline size as a function of heat treatment conditions is shown in Fig. 4-60. The nanocrystals had a size of about 10 nm initially and stabilized at a size of 30 nm, the growth rate after the size of 20 nm was slow. This can be attributed to a high nucleation density coupled with a rejection of solute to the residual amorphous matrix. This reduces the driving force for further nucleation and growth, thus stabilizing the microstructure. Ping [183] has reported the composition difference in primary crystals and remaining amorphous matrix of $\text{Co}_{44}\text{Fe}_{44}\text{Zr}_7\text{B}_4\text{Cu}_1$ alloy: Zr-enriched residual amorphous phase and Zr-depleted crystals. The Zr enriched residual amorphous phase will be a composition barrier for further growth of primary crystals. The size of nanocrystals exhibited a Gaussian distribution (Fig. 4-61 and Fig. 4-62). For longer annealing time, the peak position shifts to larger size and the size distribution range became narrower. The difference of size distributions at 450 °C and 600 °C is that the peak position of distributions from the sample heat treated at 600 °C was at larger size than at 450 °C; however the size distribution ranges were very close at these two temperatures.

For higher temperature annealing, with increased diffusion, the residual amorphous matrix crystallized, this secondary crystallization was a heterogeneous nucleation process possibly produced by consuming the inter-crystal residual amorphous phase. However, due to the very high density of primary crystals, and the more Zr-enriched regions surrounding the crystals, the grain growth was slow even at the high temperature of 600 °C. This stability will be very useful for high temperature applications of this alloy.

5.3.5 Magnetic properties

The saturation magnetization (M_s) increased after crystallization. As shown in Fig. 4-66, for samples annealed at 600 °C, the saturation magnetization increased by about 10 % compared to the amorphous ribbon. However, the hysteresis loop of the sample annealed

at 600 °C for 1440 min (Fig. 4-66), showing smaller squareness of the loop and larger coercivity, indicates that some of the soft magnetic properties deteriorate after this long time and high temperature annealing. This deterioration is due to secondary crystallization and surface oxidation, as well as an increase in crystal size (as suggested by Herzer model [4]). The situation for samples annealed at low temperatures or shorter time was better. An example was provided in Fig. 4-66: a small increase in both squareness of the loop and coercivity were observed for the sample annealed at 600 °C for 240 min. Significantly, for the crystallized samples, the saturation magnetization generally increases (Table 4-8); the coercivity did not increase much except for the 600 °C 1440 min annealed sample (Table 4-8). This improvement in soft magnetic properties could be attributed to nanocrystalline formation.

The saturation magnetization as a function of crystalline volume fraction shows that M_s increases with increasing crystalline volume fraction (Fig. 4-67 (a)); the relationship is consistent with the relationship that magnetization in a material is the weight ratio sum of magnetization of the phases included in the materials. The coercivity was plotted as a function of crystal size (Fig. 4-67 (b)), which showed that with the increasing crystal size, the coercivity decreased. However, from the Herzer model [4], in the size range selected, the coercivity should be proportional to (precipitate size)⁶. This difference in behavior was due to the precipitate density effect, since the interaction between the nanocrystalline precipitates will be weak if the neighboring precipitate distance is larger than the exchange length. The low density of nanoprecipitates induced high coercivity in the sample although the precipitate size was about 10 nm. In Kulik's paper on the microstructural correlation with magnetic properties of Finemet alloys [167], magnetic hardening for very low density of nanocrystals was observed and modeled. From this point of view, in order to further improve the soft magnetic properties in this $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ magnetic alloy, higher temperature short time annealing can be selected to produce high-density nanocrystalline material.

5.3.6 Summary of the nanocrystallization process, magnetic properties in Cu free HiTperm alloy $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$.

From the above discussion, the nanocrystallization process in $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous precursor can be described as: (a) precipitation of nanograins about 10 nm in size; (b) dendritic growth and formation irregular shaped grains; (c) heterogeneous nucleation and growth of secondary phase; (d) precipitation of $(\text{Fe}, \text{Co})_3\text{Zr}$ phase. The magnetic properties deteriorated at the first stage of formation of low density nanoprecipitates, improved after formation of high density of nanoprecipitates and deteriorated again for the secondary crystallization event. Combined with the investigation work of Cu containing HiTperm alloy [7, 9], the crystallization process and magnetic properties evolution is summarized in the following flow chart (Fig. 5-15).

Fig. 5-15 Nanocrystallization behavior of Cu free HiTperm alloy $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$.

5.4 Mechanical alloying of processing Co-Fe based nanocrystalline soft magnetic materials

Co-Fe based magnetic alloys have highest saturation magnetization among the existing magnetic materials. Formation of desirable nanostructures as in HiTperm alloys can improve the soft magnetic properties. In this section, formation of nanostructures in Co-Fe based alloys by MA is discussed. The alloying process, microstructural evolution during the milling, the effects of additional elements on the alloying process and microstructures was investigated. It was found that nanostructures formed after sufficient long time of milling. The as milled alloy powders were not magnetically soft, however, annealing effectively improved the soft magnetic properties. A comparison of the microstructures and magnetic properties of MA Co-Fe based alloys with that of HiTperm alloys was carried out.

5.4.1 The alloying process of $\text{Co}_{50}\text{Fe}_{50}$

During the high energy BM of ductile materials, the powders are repeatedly flattened, cold welded, fractured and re-welded [25]. The starting elemental powders Fe and Co have different shapes, i.e., Fe particles have an irregular shape and Co particles have a spheroidal shape (Fig. 4-68 a&b). After 25 min milling with a speed of 300 rpm (Fig. 4-68 c), it is difficult to distinguish these two elemental particles directly from SEM morphological observations; the size of the particles also decreased significantly. From the elemental maps in Fig. 4-69 (a), it is clear that Fe and Co had not yet mixed since they had quite different maps of Fe and Co. Thus at this stage, cold working and fracture were dominant compared to alloying. After milling at 300 rpm for 50 min, increase of particle size (Fig. 4-68 d) and some overlap of the elemental maps of the elemental distribution of Fe and Co (Fig. 4-69 b) indicated that mixing of Fe and Co had proceeded to some extent. In Fig. 4-69 (b), each individual particle consisted of two regions: one was Fe rich and one was Co rich. After milling at 300 rpm for 100 min (Fig. 4-68 e), the significant

increase of particle size and surface morphology change as well as the near correlated elemental maps of Fe and Co suggested that from 25 min to 100 min of milling, cold welding and fracture were dominant, which led to mixing and alloying of Fe and Co. After milling at 300 rpm for 200 min, the particle size decreased again; the map of Fe and Co was almost the same (Fig. 4-69 d), mixing of Fe and Co was thus completed for 200 min of milling. At this stage of milling, fracture of powders was dominant.

The XRD result of powders, which had undergone short periods of milling (Fig. 4-79 a –e), also reflected this alloying process. In Fig. 4-79 (b), which shows the XRD result of powders which underwent 25 min of milling, the b.c.c Fe and h.c.p Co peaks could be distinguished and the b.c.c Fe was sharp; but compared to the peaks of the premixing powders, the Fe peaks was relatively broad for powders milled at 300 rpm for 25 min, the intensity of both Fe and Co peak also decreased significantly. This means that milling had introduced defects in the powders but alloying had not yet begun. For 50 min and 100 min further milling at 300 rpm (Fig. 4-79 c and d), broadening of original Fe peaks and a decrease in intensity of both Fe and Co peaks was observed. After 100 min of milling, the Co peaks almost disappeared. A deviation from the Fe peaks was observed for powders that underwent 100 min and 200 min milling; thus the XRD results indicated that an alloying process had begun for 100 min and 200 min milling.

From the above analysis, the alloying process can be simply described as: (a) flattening and fracturing of elemental particles; (b) cold welding and mixing of Fe and Co particles; (c) homogenization of composition, alloying and fracture of alloyed particles.

5.4.2 Effect of P and B on the alloying process

The starting materials FeP and FeB are brittle. The alloying of the multi-component $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ was thus more complex than the alloying of $\text{Co}_{50}\text{Fe}_{50}$, it will include the reactions of ductile Fe with ductile Co and ductile Fe, Co with brittle FeP, FeB. From the

morphological observations of short time milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ particles (Fig. 4-72) it

decrease of particle size, increase to a very large size and decreased again. However, comparing the particles undergone the same milling time (Fig. 4-68 and Fig. 4-72), $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ particles had a smaller size than $\text{Co}_{50}\text{Fe}_{50}$ particles. This suggested that with the addition of P and B, welding was reduced during milling and alloying would be slowed down. The XRD results of short time milled powders also reflected that alloying of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ (Fig. 4-80 a-e) was slower than $\text{Co}_{50}\text{Fe}_{50}$ (Fig. 4-79 a-e).

In order to alloy FeP and FeB into the Co-Fe alloys, the FeP and FeB particles are required to be trapped by the ductile Co and Fe particles. This trapping process reduced the contacting surface of ductile Co and Fe particles, thus alloying between Co and Fe slowed down. Welding was also less effective than milling of Co and Fe particles because of the brittle FeP and FeB. Increased amount of FeP and FeB in the starting material affected the alloying to a greater extent. From Fig. 4-81 (b), it can be seen that some Co particles remained unreact after 15 h milling at 300 rpm in $\text{Co}_{41.5}\text{Fe}_{41.5}\text{P}_{14}\text{B}_4$ particles.

5.4.3 The particle size of $\text{Co}_{50}\text{Fe}_{50}$ powders

For longer periods of milling at 300 rpm, the particle size of $\text{Co}_{50}\text{Fe}_{50}$ powders decreased with milling time, as shown in Fig. 4-70. However, the morphology of the particles did not change much during this reduction of particle size. The particle size distribution in Fig. 4-71 indicated an effective reduction of particle size during milling, especially after 10 h and 15 h of milling. As listed in Table 4-9, after 5 h milling, the particle size has a wide distribution range from 5 μm to more than 30 μm . After 15 h milling, the particle size distribution range was much smaller, i.e., from 2 μm to 16 μm ; for 20 h – 70h milling, the particle size distribution range became narrower.

The mean particle size calculated from the average diameter of particles shows a decrease in particle size with milling time in the range of 5 h ~ 70 h (Table 4-9). As in the case of the particle size distribution range, decrease in mean particle size was significant for 10 h and 15 h milling; however further milling at 300 rpm did not decrease the mean particle size much; even up to 70 h milling the particle size was 3.3 μm . An increase in

From this particle size and distribution range analysis, it was concluded that on further milling after alloying of $\text{Co}_{50}\text{Fe}_{50}$, fracture was dominant and cold welding was not effective. This may be due to the fact that the alloyed phase was not ductile. As the particle size is reduced, further fracture will need higher energy of milling; therefore the reduction of particle size was slow in the later stage of milling.

As discussed in section 5.4.2, P and B additions slowed down the alloying process. After the elements in the brittle particles diffused into the ductile particles during further milling, their effect on the contacting of particles for alloying and cold welding will disappear. However, it was found that the alloy powders with P and B additions were much smaller than $\text{Co}_{50}\text{Fe}_{50}$ particles undergone same time of milling.

Fig. 4- 75 showed the particle morphology of as milled $\text{Co}_{4.2.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$ powders. The morphology of 5 h milled $\text{Co}_{4.2.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$ particles was similar to that of 100 min milled $\text{Co}_{50}\text{Fe}_{50}$ particles, suggesting a slow alloying rate in milling of $\text{Co}_{4.2.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$ powders.

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Fig. 4-76 showed the morphology of as milled $\text{Co}_{41}\text{Fe}_{41}\text{P}_{14}\text{B}_4$ particles. The morphologies of 5 h and 10 h milled $\text{Co}_{41}\text{Fe}_{41}\text{P}_{14}\text{B}_4$ particles similar to that of 5 h and 10 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ particle. However some faceted large particles were observed in 15 h milled $\text{Co}_{41}\text{Fe}_{41}\text{P}_{14}\text{B}_4$ particles (Fig. 4-76 c); formation of these particles was due to the sticking of the small particles (cold welding effect) and fracture of the large particles.

From the morphological evolution of particles with P and B additions, the following conclusions can be drawn: addition of P and B can (a) effectively reduce the particle size of Co-Fe alloys, (b) slow down the alloying process in the initial stage, (c) boron can play a role in the formation of spheroidal powders with uniform small size; (d) phosphorus can increase the ductility of powders, which led to a significant cold welding in the later stage of milling.

5.4.5 Milling speed on the particle morphological evolution

It is well-known that milling speed has a significant effect on alloying. Below some speed of milling, alloying may even not occur [25]. Here the effect of milling speed on morphology of $\text{Co}_{50}\text{Fe}_{50}$ particles and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ particles was investigated after pre-milling of 5 h at 300 rpm.

From the morphology of 200 rpm further milled $\text{Co}_{50}\text{Fe}_{50}$ particles after 300 rpm 5 h milling (Fig. 4-77), it can be seen the particle size of alloyed powders (5 h milling at 300 rpm) decreased more sharply after milling at 200 rpm compared at 300 rpm (Fig. 4-70). After further milling for only 5 h at 200 rpm, the particle size was comparable with the particles milled for 50 h at 300 rpm. The average size of powders further milled at 200 rpm for 5 h, 10 h and 15 h was 4.9 μm , 4.1 μm and 3.7 μm respectively.

The morphology of 200 rpm milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ particles (Fig. 4-78) was similar to the 300 rpm milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ particles (Fig. 4-73). The $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ alloy powders after further milling at 200 rpm had a broader size distribution range than those after 300 rpm milling (Table 4-11). The particle size and size distribution range (Table 4-11) did not change with milling time at 200 rpm for $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ alloy powders.

The greater effectiveness of low milling speed of 200 rpm in reducing the particle size of $\text{Co}_{50}\text{Fe}_{50}$ alloy was due to the milling mechanism at low milling speed. At low speed, shearing of particles was dominant, while at high speed, impaction was dominant. With a decrease in particle size, shearing of particles became difficult and required higher energy, therefore both for $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders, the decrease of particle size for 10 h and 15 h milling at 200rpm was not as fast as the first 5 h milling.

5.4.6 Microstructural evolution

TEM observations of the microstructural evolution of the particles revealed refinement of the microstructure due to long milling time.

For the $\text{Co}_{50}\text{Fe}_{50}$ powders, a coarse banded microstructure was observed after 5 h and 10 h milling at 300 rpm (Fig. 4-82 a & b). Initially the banded microstructure was regular, with a wavelength of about 30 nm and a length reaching the edge of particles (Fig. 4-82 a). However, when the particles underwent 20 h milling (Fig. 4-83 c), break up of the bands was observed; the bands were about 30 nm in wavelength and about 100 nm in length. These smaller bands were more randomly arranged than the initial bands of the particles milled for 5 h and 10 h. For particles milled for 70 h (Fig. 4-82 d), the banded microstructure disappeared. The break up of the banded structure was attributed to the introduction of more energy and defects into the particles during milling. From the dark field image and SADP (Fig. 4-82 e), the banded microstructure consists of small grains, many of which show texture effects. Such banded microstructures have been generally observed in MM ductile particles, e.g. Ag-Cu system; and were considered to be a composite lamellar structure of the constituent elements [25]. However from EDX composition analysis of two neighboring bands (Table. 4-12), the bands are not composites of individual elements. Although composition inhomogeneity does exist among the particles tested, neighboring bands have similar compositions, the SADP analysis also indicates that the alloy has formed at this stage of milling. As discussed in Section 5.4.1, alloying has taken place after 50 min milling at 300 rpm and particle size

decreased for further milling after 100 min, the texture was considered to be induced by work hardening or shearing of alloyed particles during high-energy MM. As the particle size decreased, work hardening and shearing needed greater amount of energy and the bands broke up by random impacts during MM. Textured microstructures were observed previously in some ball milled alloy powders, such as Fe-Ta [90] and Al-Mg-Sc [91]; formation of the lamellar structure was reported to occur due to cold working induced by milling and it was an intermediate process in refinement of microstructures [91].

The XRD results of Co₅₀Fe₅₀ powders 5 h to 70 h milled at 300 rpm (Fig. 4-79) did not show any phase transformation during milling. Further, no obvious difference in peak broadening was observed. The XRD results of Co₅₀Fe₅₀ powders can be correlated to TEM microstructural observations: when the banded structure was coarse, it consisted of

milled powders showed a relative homogeneous ring pattern of α -(Co, Fe) phase (Fig. 4-83 f). No additional phase was detected from SADP analysis of 20 h milled powders. For 5 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders, extra spots besides the ring pattern of α -(Co, Fe) phase were observed (Fig. 4-83 e), which can belong to the un-alloyed Co phase.

The crystalline phase of powders milled for 5 h to 70 h consisted of only α -(Co, Fe) phase (Fig. 4-80). It can be seen that the peaks from MA $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ were generally broader than those from $\text{Co}_{50}\text{Fe}_{50}$ powders. With an increase in milling time, the peaks appeared to be broader for $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders, suggesting the refinement of microstructure by milling. This is consistent with the TEM microstructural observations. Besides the α -(Co, Fe) phase peaks, a broad hump was also observed for long time milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders (e.g., the circled hump in Fig. 4-80 (k)), this hump was from the amorphous phase in the powders. The DSC result (Fig. 4-84) of 70 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders also showed a crystallization exothermal peak at around 440 °C.

The microstructural analysis of the MA $\text{Co}_{50}\text{Fe}_{50}$ powders and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders indicated that P and B additions aided in refinement of microstructures and formation of nanocrystals. The effect of P and B on the microstructure was due to the brittleness of alloy powders with P and B. The brittleness led to the formation of small sized particles and made shearing of particles difficult. Therefore in $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ particles, banded microstructure was only observed in the 5 h milled powders. With a decrease in particle size, shearing became ineffective and impact was dominant. Break up of banded microstructure and formation of spheroidal crystals then occurred for further milling in both $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ and $\text{Co}_{50}\text{Fe}_{50}$ alloys. Because of their smaller size, it was easier for $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders to form nanocrystalline microstructure compared to $\text{Co}_{50}\text{Fe}_{50}$ powders. This analysis suggested that in both $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ and $\text{Co}_{50}\text{Fe}_{50}$ alloys, nanostructures can be processed by high energy MM.

P and B additions aided in the amorphization of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders. The formation of the amorphous phase improved the ductility of fine powders. Therefore, in

both $\text{Co}_{42.5}\text{Fe}_{42.5}\text{P}_7\text{B}_8$ and $\text{Co}_{41}\text{Fe}_{41}\text{P}_{14}\text{B}_4$ powders, an increase in powder size was observed after 15 h and 10 h milling respectively (Table 4-10).

The morphology of nanocrystals formed in MA Co-Fe based alloys was different from that formed by crystallization of melt-spun Co-Fe based HiTperm amorphous precursors. MM led to the formation of spheroidal shaped nanocrystals and crystallization formed irregular shaped nanocrystals. This is due to the different mechanisms of formation of nanocrystals in these two techniques: for MM the nanocrystals were formed by impaction during milling and for crystallization nanocrystals was formed by nucleation and growth mechanism. A detailed discussion of these two techniques is given in section 5.5.

5.4.7 Magnetic properties of as milled powders

For Co-Fe based magnetic powders, it was found that the as milled powders were not magnetically soft and heat treatment improved the magnetic properties from VSM results.

Fig. 4-85 showed the magnetic properties evolution with milling time of $\text{Co}_{50}\text{Fe}_{50}$ powders. It can be seen that the saturation magnetization (M_s) increased after milling and the coercivity (H_c) increased significantly with milling time. The premixed powders had a M_s of 1.83 T, which was very close to the weighted average of M_s of pure Fe and Co powders. A small decrease in M_s of $\text{Co}_{50}\text{Fe}_{50}$ powders milled for 25 min was due to the inhomogeneity in composition. A small increase was observed in the M_s for $\text{Co}_{50}\text{Fe}_{50}$ powders milled for 50 min and 100 min. This indicated that alloying has occurred on the surface where Fe and Co impinged although they had not yet completely mixed. But from 100 min to 10 h milling, a large increase in M_s was observed, especially from 100 min to 200 min milling time; this reflected a true alloying process. The M_s reached its highest value for 10 h milling, which was 2.24 T. This value is very close to that reported by Lee [107]. The M_s did not vary much for 15 h – 70 h milling. From this point of view, the homogenization of the alloy compound was not completed for 200 min milling, although from the EDX elemental mapping, the two elements Fe and Co appeared to mix completely; the time required for homogenization was 10 h of milling at 300 rpm. From

the M_s data and analysis, the alloying process of $\text{Co}_{50}\text{Fe}_{50}$ can be further confirmed to be: premixing (flattening and fracture of elemental powders, 25 min milling); mixing and alloying (50-200 min); and composition homogenization (after 5 h milling).

As in Ref. [102-108], due to large strains incorporated into powders during milling, the as milled $\text{Co}_{50}\text{Fe}_{50}$ powders have much larger coercivity compared to the commercial Co-Fe magnetic alloys (Fig. 4-85). For longer milling time, coercivity increased significantly. This was because more defects, surface oxidation and contamination were induced for longer milling time. These undesirable introductions were more serious when the ball to powder weight ratio was higher, as reflected by the abnormal increase of coercivity for 200 min milling. Meanwhile, the observations of the microstructures of the as milled $\text{Co}_{50}\text{Fe}_{50}$ powders showed that large coercivity could also be caused by the formation of banded structures, which consists of grains showing texture effects. The Herzer model [4, 43] at this size range showed that the coercivity may reach a maximum. From Fig. 4-85, it can be also seen that the coercivity decreased when the banded structure disappeared for 70 h milling (Fig. 4-82 d). Therefore, to process magnetically soft Co-Fe alloy, the banded microstructure should be avoided by long time of milling.

As in MM $\text{Co}_{50}\text{Fe}_{50}$ powders, the as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders showed an increase of M_s and H_c after milling (Fig. 4-86). The premixed $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders had a M_s of 1.49 T. There are four steps in the M_s v/s milling time curve: increase slowly from 25 min to 100 min milling; increase dramatically to 1.90 T after 10 h milling; minor decrease for 15 h and 20 h milling; increase again from 20 h to 70 h milling. The M_s of 70 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders was 1.92 T. The H_c of premixed $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders was close to the premixed $\text{Co}_{50}\text{Fe}_{50}$ powders, about 3210 A/m. An increased to 6910 A/m of the H_c of 25 min milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders was due to an allotropic transformation of Co powders induced by milling [240]. From 50 h to 100 min milling, the H_c of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders increased significantly with milling time. Further milling after 200 min decreased the H_c of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders, which was different

from milling of $\text{Co}_{50}\text{Fe}_{50}$ powders. The decrease of H_c with milling time was due to the refinement of microstructure as well as formation of amorphous phase (see discussions in section 5.4.5).

Although the as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders had a nanocrystalline structure, which was expected to have a better soft magnetic properties than as milled $\text{Co}_{50}\text{Fe}_{50}$, it was found that the coercivity of as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders was generally higher than that of as milled $\text{Co}_{50}\text{Fe}_{50}$ powders. The reasons can be: (a) the powder with nanocrystalline structure was still highly stressed, as can be seen from the DSC result of 70 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders which shows a large stress relaxation hump similar to 70 h milled $\text{Co}_{50}\text{Fe}_{50}$ (Fig. 4-84); (b) the alloy with P and B additions is intrinsically magnetically harder than the $\text{Co}_{50}\text{Fe}_{50}$ alloy; (c) the surface of the small sized $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders pinned magnetic domains more seriously than the relative larger sized $\text{Co}_{50}\text{Fe}_{50}$ powders. The different behavior of the coercivity variation with milling time in $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ and $\text{Co}_{50}\text{Fe}_{50}$ powders indicated that the formation of nanocrystalline structure is effective in reducing the coercivity, which is consistent with the Herzer model [4, 43].

5.4.8 Improvement of soft magnetic properties through heat treatment

The large stress in the as milled powders was the main reason for the inferior magnetic properties. From the DSC results (Fig. 4-84), the stress relaxation occurred at the temperature range of 300 °C to 600 °C. Heat treatment was thus carried out at temperatures within the stress relaxation temperature range. It was found for both $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ alloy powders, the magnetic properties improved significantly after heat treatment (Fig. 4-87 and Fig. 4-88)

From Fig. 4-87, it can be seen that coercivity of MA $\text{Co}_{50}\text{Fe}_{50}$ powders decreased with increasing heat treatment temperature. After heat treatment at 350 °C for 2h, the H_c decreased sharply from 5400 A/m to 1110 A/m for 20 h, 300 rpm milled powders; higher temperature than 350 °C of heat treatment decreased H_c further. Similar significant

decrease of H_c through heat treatments also observed in 70 h milled and 5 h (300 rpm)+15 h (200 rpm) $\text{Co}_{50}\text{Fe}_{50}$ powders. The magnetization of 300 rpm 20 h and 70 h milled powders did not vary much after heat treatment, however the magnetization of 5 h (300 rpm)+ 15 h (200 rpm) increased significantly with an increase in heat treatment temperatures. This indicated that (a) alloying was not completed after 5 h (300 rpm)+ 15 h (200 rpm) milling of $\text{Co}_{50}\text{Fe}_{50}$ powders, (b) heat treatment aided in the homogenization of composition and (c) low temperature (350 °C and 400 °C) heat treatment involved only a short diffusion distance. From TEM microstructural observations, the 20 h as milled particles had a randomly arranged banded microstructure (Fig. 4-82 c); the 70 h as milled particles showed a nanocrystalline microstructure (Fig. 4-82 d). Since low speed of milling has less effect on the microstructure, it is expected that 5 h (300 rpm)+ 15 h (200 rpm) milled $\text{Co}_{50}\text{Fe}_{50}$ powders had a microstructure similar to 5 h 300 rpm milled $\text{Co}_{50}\text{Fe}_{50}$ powders (Fig. 4-82 a). The coercivity of 5 h (300 rpm)+ 15 h (200 rpm) milled $\text{Co}_{50}\text{Fe}_{50}$ powders was thus the largest among the heat treated $\text{Co}_{50}\text{Fe}_{50}$ powders because of the coarse microstructure. For 20 h and 70 h milled $\text{Co}_{50}\text{Fe}_{50}$ powders, the coercivity was determined by stress relaxation and coarsening of microstructure after heat treatments. Therefore, the coercivity of 20 h milled powders was slightly smaller than 70 h milled powders after 350 °C, 400 °C and 450 °C heat treatment since at these temperatures stress relaxation was dominant and 70 h powders were in higher stress state. The small increase in coercivity of 20 h milled $\text{Co}_{50}\text{Fe}_{50}$ powders (Fig. 4-87) after heat treatment at 500 °C was due to coarsening of the microstructure which led to inefficient exchange coupling. The H_c of 70 h milled $\text{Co}_{50}\text{Fe}_{50}$ powders decreased after 500 °C heat treatment; this is due to the nanocrystalline structure in these powders.

The variation of magnetic properties with heat treatment temperature was complex in MM $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders. As discussed above, this variation was caused by stress relaxation, homogenization of composition, coarsening of microstructure, crystallization and formation of magnetic hard phases in the MM $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders. For heat

treatment at 350 °C for 2 h, the $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders showed a small increase in M_s and significant decrease of H_c , indicating that 350 °C heat treatment mainly involved stress relaxation and homogenization of composition. The $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders showed a very small H_c of 970 A/m and a slightly decreased M_s after heat treatment at 400 °C for 2 h. The significant improvement in soft magnetic properties was due to the fine nanocrystals (the grain size was about 15 nm in the 70 h 300 rpm as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders from TEM observations) and amorphous phase. Heat treatment at 400 °C reduced the stress without serious coarsening of microstructure; it also induced change in the compositions of the phases and decreased the M_s . The DSC result of 70 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders indicated that the crystallization event occurred at 445 °C (Fig. 4-84). Therefore the magnetic properties deteriorated after 450 °C and 500 °C heat treatment due to crystallization of the amorphous phase and coarsening of nanocrystalline structure. The magnetization of 70 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders increased slightly after 450 °C heat treatment, due to the crystallization of amorphous phase; it then decreased after 500 °C heat treatment, which was probably due to precipitation of nonmagnetic phases such as phosphide and boride. The 300 rpm 20 h milled and 5 h (300 rpm)+ 15 h (200 rpm) milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders showed similar magnetic properties after 400 °C, 450 °C and 500 °C heat treatment. This was due to the similarity in the microstructures of these powders: in both 300 rpm 20 h milled and 5 h (300 rpm)+ 15 h (200 rpm) milled powders there was some unalloyed FeP and FeB, they served as the nuclei for the precipitation of these phases during heat treatments. Due to the high stress and relatively coarse microstructure in 5 h (300 rpm)+ 15 h (200 rpm) milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders, 5 h (300 rpm)+ 15 h (200 rpm) milled powders generally had a little smaller magnetization and larger coercivity than 20 h 300 rpm milled powders.

The above analysis of magnetic properties of as milled $\text{Co}_{50}\text{Fe}_{50}$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powder indicated that magnetic properties of MM Co-Fe based alloy powders are determined by residual stress and microstructural features.

5.5 Comparisons of soft magnetic materials prepared by crystallization and by mechanical alloying

The investigations of melt spun and mechanical alloyed Co based and CoFe based magnetic alloys showed a number of common points in these magnetic alloys: the microstructural dependence of magnetic properties; the crystallization of amorphous phases; the coarsening of nanostructures; and the magnetization of mechanically milled powders. These common points arise from their intrinsic correlations. A comparison of these magnetic alloys, including crystallization behavior, formation mechanisms of microstructures and magnetic properties, is included in this section.

5.5.1 Crystallization behavior

Amorphous alloys are metastable; they will crystallize when the energy barrier is overcome at elevated temperatures or other external conditions. The thermodynamic driving force for crystallization is the energy difference between equilibrium crystalline phases and amorphous phase. Crystallization is realized through the rearrangement of atoms, which is a kinetic process. Composition of amorphous alloy determines their equilibrium crystallization products; diffusion of atoms determines the process of formation of these equilibrium products; the composition can also play an important role in the diffusion of atoms. Therefore, the crystallization products are sensitive to alloy composition and heat treatment conditions.

From section 4.1 and 5.1, the Co based $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ amorphous alloys first crystallized into a metastable crystalline phase with a composition similar to the amorphous matrix or into h.c.p Co phase at elevated temperatures. From section 4.3 and 5.3, it is known that the Co-Fe based copper free HiTperm alloy first crystallized into b.c.c. (Co, Fe) phase. In the crystallization of other metallic glasses, such as Ni-Ti-B glass with near ternary eutectic composition [145], Zr-Cu-Ni-Al [152], (CoCr)SiB [208] and Fe-Si-B [239], it was also found that the first crystallization products have similar

composition to the amorphous matrix. This indicates that in the first stage of crystallization from amorphous alloy, the atoms will select the quickest route to form a crystalline phase and reduce the energy, thus crystallization from metallic glass is different from crystallization in conventional solidification from the melt.

It is also interesting to see that the strongest crystalline peak for the first stage of crystallization is always positioned within the range of the hump in the XRD data. For the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}$ alloy, the strongest peaks for the metastable crystalline phase are at 44.8 and 46.0 degree respectively and the amorphous hump is at the range of 40 to 50 degree (XRD, Cu target). It is same for the $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy, which has the strongest crystalline peak at 44.8 degree. This indicated that the atomic arrangement in crystalline phase is related to the topological short range ordering in amorphous alloy, and that crystallization is actually the rearrangement of atoms within a small region.

The nucleation density is related to the critical free energy change and activation energy, lower activation energy has higher chance to form high density crystals from amorphous matrix. The activation energy for crystallization of metallic glass $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ is 7.1 eV/atom, doubled that of Finemet, Nanoperm and HiTperm alloys (activation energies for crystallizations are around 3-4 eV/atom), the nucleation density was thus very low for crystallization of metallic glass $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$.

Comparison of crystallization behaviors of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloys aided a deeper understanding of amorphous alloys. Design for nanocrystallization from amorphous alloys thus can be from choosing the appropriate composition to allow formation of desirable crystalline phase, bonding of the crystalline phase to allow a lower interfacial energy, addition of dissimilar atoms to suppress grain growth, and increasing the number of nucleation sites to form high density of nanocrystals.

5.5.2 Amorphization by rapid quenching and mechanical alloying

Rapid quenching implies “quenching” in the state present in the melt, using the idea that diffusion is suppressed at low temperatures. Therefore phase separation and

crystallization is difficult and an amorphous phase form. Using this principle, all metals and alloys can be prepared in amorphous state when the cooling rate is high enough [63].

Mechanical amorphization process is different from rapid quenching, it works through absorption of mechanical energy. The mechanism for amorphization by MM has not been established [25]. From the investigation of MA Co-Si-B amorphous alloys, it showed that (a) the amorphous phase was formed directly without formation of crystalline alloy and (b) the early formed amorphous phase had a higher crystallization temperature. Two points can thus be inferred: (a) amorphization is related to the interfacial reaction and (b) amorphous is a metastable state. The realization of amorphization by MA is through collision and mixing of atoms. Fig. 5-16 shows schematically such a reaction process. The atoms will be shifted away from their initial lattice points after impact during MM; they will then be trapped by other atoms. The trapped atoms can be located at new lattice points which may cause lattice distortion; they can also be located at some random place, and if sufficient random atoms accumulate an amorphous phase will form. As in rapid quenching from the melt, such a metastable state is difficult to reach if the atoms are of similar size. Since amorphization by MA is through impact and trapping of atoms, the amorphous phase formed by MA can be in a larger composition range than by rapid quenching. This also explains that why equiatomic binary amorphous alloy can be easily formed by MA but not formed by rapid quenching. The distance that atoms can move during impact depends on three factors: impact intensity, the energy barrier for the atoms escaping from the initial lattice and the barrier met by the atoms during its proceeding. Therefore if milling energy is too low, it is difficult to amorphize or alloy. For Co-Si-B based alloys, due to the different sized atoms and easily reached metastable amorphous state, amorphization occurred very fast by MA. Fe and Co have very close atomic size and Co atoms can substitute Fe atoms easily, therefore amorphization was difficult and was never observed in MA of Co-Fe alloy. With the small amount of addition of P and B, it can only form a small amount of amorphous phase after long time high intensity MM.

Fig. 5-16 Amorphization by mechanical milling. Black ball and white ball represents different type of atoms

The impact can be considered as introduction of shock wave to the powders. The energy of shock wave is partially absorbed by the atoms as kinetic energy and partially converted to the heat during collision of atoms. The shock wave characteristics of mechanical impact are comparable with ion implantation (or other irradiation technique).

The similarity of rapid quenching and MA in the easy amorphization composition range indicated that the amorphous phase is a state of a solid. At high temperatures (melt) and during the impact, the atoms are in a high energy state and away from the position of minimum energy (Fig. 5-17). In Fig. 5-17, position “1” and “2” represents the crystalline and amorphous state respectively. After quenching and impact, the atoms will go to lower energy state, which can be position “1” or “2”. Since position “1” has lower energy than

Fig. 5-17 Schematic process of atoms reaching the equilibrium state for (a) materials of difficult amorphization and (b) materials of easy amorphization. X represents the distance from the position of minimum energy, E represents the energy.

“2”. The thermal vibration of atoms will lead to the minimum energy state “1”, which is the case of slow cooling. However, if the thermal vibration was suppressed, the atoms would drop directly to the low energy state, depending on the distance for them to reach the state, as shown in Fig. 5-17. Materials which can be easily amorphized have a wide range of region “2” and a slim range of region “1”. The composition that contains a number of atoms with different size corresponds to a wide range of region “2”.

5.5.3 Nanocrystalline structure formed by crystallization and mechanical alloying

Both crystallization from amorphous precursors and MA have successfully yielded nanostructures. Nanocrystallization conforms to the principle of nucleation and grain growth, which adopts methods of increasing nucleation density and suppressing grain growth during crystallization. Therefore nanocrystallization has only been observed in a few alloy systems. MA is capable of producing nanostructures in a wide range of metals, intermetallics and alloys [25].

Since crystallization is driven by the free energy difference between crystalline phase and amorphous phase, the grains can have specific morphologies and compositions. The amorphous phase is macroscopically homogeneous; therefore the nucleation from amorphous alloy is random without any crystallographic relationship, resulting in macroscopically homogeneous properties. The exceptions are surface crystallization and thin foil crystallization. The lattice strain, stress and crystallographic anisotropy are also averaged out in the whole sample due to their homogeneity.

MA of nanocrystals is through introduction of disorder into the lattice, deformation of lattice and recrystallization [25]. The nanocrystals from MM generally have a spheroidal

homogeneous in the whole material except for incomplete mixing. From this point of view, the nanocrystals formed from MM are highly unstable. The DSC results (Fig. 4-82) reflected the unstable characteristics of MA nanocrystals, which showed the exothermal humps starting from low temperature of about 300 °C. (The DSC results indicated that the temperatures reached during MM are about 300 °C). It was also observed that the powders showing large exothermal hump could be easily sintered, suggesting easy transportation of atoms in the MA crystalline powders.

Therefore, it can be concluded that crystallization from the amorphous alloy is more efficient in producing desirable magnetic structures than MA.

Low temperature annealing of MA nanocrystalline powders can sometimes effectively release the stress in the powders. However the weak texture of nanocrystals in the MA powders cannot be removed through annealing, which is undesirable for magnetic properties. The only pathway to reduce texture is high energy and long time milling. Therefore, the 70 h milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ powders showed good soft magnetic properties after annealing at 400 °C for 2 h.

5.5.4 Microstructure and magnetic properties

From the discussions in sections 5.1, 5.2, 5.3 and 5.4, the magnetic properties can be correlated with the microstructure. The microstructures can be divided into four types: amorphous, nanocrystalline, stressed nanocrystalline and coarse grained microstructures. The magnetic properties discussed here include magnetization and coercivity.

The amorphous alloy has lowest H_c among the four microstructures for both ribbon and powder materials. The H_c is less than 80 A/m around 800 A/m respectively for amorphous ribbons and powders. The larger H_c of MA amorphous powders was due to pinning of magnetic domains by surface, some unalloyed and heterogeneous crystallized crystalline phases. The M_s of the amorphous alloy is relatively low. For amorphous $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy, the M_s is larger than that of the crystalline counterpart. However, MM decreased the M_s through amorphization of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy, indicating a

special electronic structure in the amorphous phase. The amorphous $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy has a lower M_s than its crystalline counterpart.

The high density nanocrystalline phase also showed a low H_c , as in nanocrystalline $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$, which is consistent with the Herzer model. The stressed nanocrystalline phase in MA Co-Fe based alloy powders had a very large H_c . The stress induced H_c in nanocrystalline structure is same as that in conventional crystalline phase. In thin film Co-Fe based alloys, it has been reported that nanocrystalline Co-Fe film was not as magnetically soft as a high density Co-Fe nanocrystals embedded in an amorphous matrix film [242]. This indicated that the small amount of amorphous phase played a significant role in obtaining superior soft magnetic properties; the amorphous phase aided in the stress relaxation in lattice or exchange coupling of nanocrystals. In MM of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ alloys, it can be seen that the H_c did not increase but slightly decreased after 200 min of further milling; the decrease of H_c can be attributed to the smaller grain size and formation of amorphous phase for longer time of high energy MM. The nanocrystalline structure can have a slightly higher M_s . E.g., the 70 h milled $\text{Co}_{50}\text{Fe}_{50}$ powders have relatively higher M_s ; the M_s of $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ increased continuously with milling time, this may also be due to the nanocrystalline structure.

The H_c of coarse grained microstructures depends on the crystallographic anisotropy of magnetic phases. In the crystallized $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy, the H_c is large. The H_c of 600 °C 24 h crystallized $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy showed much smaller H_c than crystallized $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy although the H_c of 600 °C 24 h crystallized $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy was much larger than its amorphous and nanocrystalline counterpart. The H_c of MA $\text{Co}_{50}\text{Fe}_{50}$ powders decreased with heat treatment temperature, indicating a conventional relation of H_c with grain size for $\text{Co}_{50}\text{Fe}_{50}$ powders.

The above discussion indicated that both H_c and M_s are microstructure sensitive for the alloys and microstructures investigated. The microstructural sensitivity of H_c depends on the nature of the magnetic phases, morphology of the phases and stress.

Chapter 6 Conclusions

Two melt spun Co based amorphous magnetic alloys were characterized. Mechanical alloying was used as a counterpart technique to process these alloys. The properties and microstructures in these alloys have been characterized using DSC, electrical resistivity, XRD, TEM and in situ TEM. The nanostructure formation by crystallization of amorphous precursors and mechanical alloying methods has been investigated.

6.1 Crystallization behavior of melt spun $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_6$ amorphous

[REDACTED]

(e) A coarse lamellar structure developed from the precipitates at the grain boundaries and within the grains by consuming the grains with the fine nanolamellae. At this time, an allotropic transformation resulted in the formation of metastable Co_3Si phase from the remaining nanolamellar grains. The metastable Co_3Si phase was then consumed by the equilibrium phases and finally, the coarse lamellar structure was transformed to equiaxed grain morphology.

(c) The magnetic properties measured by VSM were found to deteriorate after crystallization, the change in magnetic properties could be correlated with the morphological evolution.

6.1.2 In situ hot stage TEM crystallization

(a) In situ hot stage TEM observations showed that foil thickness played a major role in crystallization. In the thin edge of foil, crystallization occurred at around 400 °C during heating. Crystallization in thin regions was faster than in thick regions.

(b) A high density of spherical h.c.p Co precipitates with a size about 10 nm were formed after holding at 400 °C for 150 s in the thin region of the foil. The thicker region slowly crystallized into highly faulted h.c.p. and f.c.c. Co phases during holding. The precipitates in the very thick regions were clustered and had an irregular morphology.

(c) The thickness dependence of the crystallization behavior was modeled and was related to the strain induced by volume change during precipitation, this effect was considered to exert a negative pressure effect on crystallization.

(d) In situ coarsening process of nanolamellar structure was found to occur in three steps: precipitation of spherical fine precipitates → continuous coarsening of the nanolamellar structure from the surface and precipitation at the grain boundaries → formation of a stable multi-phase structure.

(e) Surface effects played a significant effect on the coarsening of nanolamellar structure in thin foils, leading to different coarsening processes in in-situ and conventional annealed samples. Considerable continuous coarsening was observed in the in situ

annealed sample, while this was virtually absent in the conventional annealed samples. However, the final products of coarsening by these two annealing methods are similar.

(f) Discontinuous coarsening from the grain boundaries was found to dominate the coarsening of the nanolamellar structure. The orientation relationship of grain boundaries with the nanolamellae and the orientation relationship of nanolamellae in the neighboring grains also affected the coarsening process.

6.2 Mechanical alloying of cobalt based amorphous magnetic alloys.

Mechanical alloying of $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ and $\text{Co}_{71}\text{Si}_{15}\text{B}_{14}$ alloys from elemental powders yielded an amorphous phase. The as milled and subsequent annealed powders were characterized using SEM, XRD, DSC and VSM.

(a) SEM results showed that alloying from elemental powders took place by fracture powders, trapping of the metalloid powders in the metal powders and diffusion. XRD and DSC results showed that formation of the amorphous phase was by direct reaction of elemental powders, rather than after crystalline phase formation, the initially formed amorphous phase was boron rich.

(b) The addition of Fe and Ni did not significantly affect the amorphization process.

(c) VSM results showed that M_s decreased with increasing milling time in the as milled powders, indicating a continuous transformation process. Annealing deteriorated the magnetic properties of these powders due to crystallization of the MA amorphous phase.

(d) It was found that the MA and the corresponding melt-spun amorphous alloys showed a number of similarities, especially in the case of the 20 h MA amorphous alloy.

6.3 Nanocrystallization of Cu free HiTperm $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ alloy

The melt spun Cu free HiTperm $\text{Co}_{44.5}\text{Fe}_{44.5}\text{Zr}_7\text{B}_4$ amorphous alloy exhibited primary nanocrystallization behavior. The nucleation, grain growth and thermal stability were investigated using DSC, electrical resistivity, XRD, TEM, HRTEM and VSM techniques.

(a) DSC and electrical resistivity showed that the crystallization temperatures of this alloy are at around 500 °C and 700 °C respectively for the primary and secondary crystallization events. From TEM analysis, it was found that in the primary crystallization event, high density α -(Co, Fe) nanocrystals formed. In the secondary crystallization event, a greater volume fraction of α -(Co, Fe) phase and a secondary phase of (Co, Fe)₃Zr formed.

(b) A detailed quantitative analysis of nucleation density, crystalline volume fraction and grain growth was carried out using TEM data coupled with the thickness measurements. A nucleation density in the order of 10^{22} m^{-3} was easily obtained in this copper free HiTperm alloy; significantly the nucleation density was high although no copper has been added to this alloy.

(c) A “cluster” morphology of nanocrystals was observed during primary crystallization, which had been speculated by other researchers to be due to several crystals closely oriented. Our HRTEM and CBED results show that, in fact, the morphology arises from single crystals. The growth of such nanocrystals followed a compact dendritic mode.

(d) It is significant to note that the growth of nanocrystals was slow when it reached a

decrease of coercivity with increasing crystalline size was observed, contrary to the expectations from the Herzer model; this was due to ineffective exchange coupling.

6.4 Mechanical alloying of Co-Fe based nanomagnetic alloys

Mechanical alloying of Co-Fe based alloys were carried out. The effect of additional elements P and B on the alloying was investigated. SEM, EDX mapping, XRD, TEM and VSM were used to characterize the as milled and annealed powders.

(a) The mixing of Co and Fe powders was completed after 200 min milling at 300 rpm with an initial increase in powder size for 50 min and 100 min milling. The powder size distribution range became narrower after milling times longer than 5 h at 300 rpm, the mean powder size also decreased. The reduction of powder size and narrowing of powder size distribution range in the milling of $\text{Co}_{50}\text{Fe}_{50}$ were more effective when milled at a lower speed of 200 rpm.

(b) From TEM analysis, a banded microstructure about 30 nm in wavelength was observed, this structure broke up on further milling and disappeared after 70 h milling. This banded structure was considered to be a texture effect.

(c) The addition of P and B affected powder size and morphology, with the addition of P and B, a smaller mean powder size and narrower size distribution was found. P and B also affected the microstructures of the as milled powders, in the 5 h mechanically alloyed $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ alloy, spherical nanocrystals with 35 nm in diameter were observed. These nanocrystals became smaller after longer time of milling.

(d) The variation of saturation magnetization as a function of milling time reflected a true alloying process. A significant increase in the saturation magnetization for milling time from 100 min to 200 min (at 300 rpm) was observed.

(e) The coercivity of as milled $\text{Co}_{50}\text{Fe}_{50}$ powders increased with milling time due to the introduction of defects, oxide and other contamination during the milling. The coercivity

of the as milled $\text{Co}_{44.5}\text{Fe}_{44.5}\text{P}_7\text{B}_4$ decreased with milling time after 10 h further milling, this was attributed to the decrease in grain size and formation of amorphous phase.

(f) Significantly, annealing substantially improved the soft magnetic properties. Thus, MA can be used for producing nanostructured soft magnetic materials.

6.5 Comparison of the magnetic materials prepared by crystallization and mechanical alloying

The materials prepared by crystallization from melt spun amorphous precursors and by mechanical alloying were compared.

(a) The study of crystallization behavior of the two Co based alloys suggested that in order to process nanocrystalline soft magnetic materials the composition should be chosen to allow the crystallization of the desired phases. The activation energy for crystallization should be relatively small to allow a high density of nucleation.

(b) The amorphous materials prepared by MA have properties similar to the corresponding melt spun ones. The formation of the metastable amorphous state was explained schematically. The nanocrystals processed by MA have a spheroidal morphology, which is different from crystallization from amorphous precursors. This was due to the different formation mechanisms of these nanocrystals. In the case of MA, introduction of defects into crystals by impaction and shearing is the dominant mechanism, while for the crystallization, high density of nucleation and slow growth is the mechanism.

(c) Finally, if the stress in the mechanical alloyed nanocrystals can be properly relieved, MA is powerful in producing nanocrystalline soft magnetic materials.

Recommendation for future work

From the investigation conducted in this project, it is significant that nanostructures can be successfully formed in the cobalt based alloys used in this project. There is still scope for further investigation. Based on the work carried out, future directions are summarized in the following.

(a) Microscopic magnetic properties of the novel nanolamellar structure in the $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ alloy and the applications. In this project, the novel nanolamellar structure was obtained and characterized, and the bulk magnetic properties were determined. However, the magnetic properties at the nanoscale are unknown. They can possibly be determined using other characterization techniques such as atomic force microscope (AFM), magnetic force microscope (MFM) and Mössbauer spectroscopy. The potential applications of the nanolamellar structure include patterned self assembly, catalysis, nanotemplates, nanogrid, etc. To make these applications into reality, a large amount of research effort is required. Among them, selective etching of the lamellar structure is very important.

(b) Mechanical amorphization: the amorphization by MA in this investigation can be extended to bulk metallic glass. Mechanical amorphization technique will be very useful in processing bulk metallic glass. Bulk magnetic metallic glass has a number of applications. The dimensions and types of bulk metallic glass are very limited so far due to the limitations of rapid cooling. Since the amorphous phase is relatively stress insensitive, the shortcoming of mechanical alloying, i.e. the large stress induced by mechanical milling, will be unimportant. However, mechanical crystallization should be avoided. Addition of surfactant and modification of milling parameters can be adopted to process fully amorphous phase. The compaction properties and low temperature sintering of the amorphous powders will be the subsequent steps to process bulk metallic glass.

(c) Processing Co-Fe based nanostructured magnetic alloys. Co-Fe based magnetic alloys have the highest magnetization among magnetic materials. From our investigation, their magnetic properties are very attractive. The investigation directions in Co-Fe based magnetic alloys can be processing of Co-Fe based alloys in other shapes and composition modification to yield spheroidal nanocrystals. For the MA technique to process Co-Fe based alloys, it is necessary to optimize the composition and milling parameters to process nanocrystals within amorphous matrix since the amorphous phase may relax the stresses in the nanocrystals; residual stresses are the main obstacle in MA processing of nanocrystalline soft magnetic alloys. A good example of the potential of this work is that of the relatively small coercivity observed in some MA Co-Fe alloy powders from this investigation.

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List of Publications

1. **Li, H.F. & Ramanujan, R.V.** (2004). Crystallization behavior of the cobalt based metallic glass $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$. *Materials Science and Engineering A*, 375-377, 1087-1091.
2. **Li, H.F. & Ramanujan, R.V.** (2004). Microstructural evolution during crystallization of a $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ magnetic material. *Intermetallics*, 12(7-9), 803-807.
3. **Li, H.F. & Ramanujan, R.V.** (2004). Microstructural evolution and nanocrystalline formation kinetics in FeCo based alloys during mechanical alloying. *Journal of Metastable and Nanocrystalline Materials*, 23, 187-190.
4. **Li, H.F. & Ramanujan, R.V.** (2004). Mechanical alloying of FeCo nanocrystalline magnetic powders. *Journal of Electronic Materials*, 33, 1289-1297.
5. **Li, H.F. & Ramanujan, R.V.** (2004). Mechanical alloying of Co-Si-B based amorphous magnetic alloys. *International Conference on Materials Processing for Properties and Performance*, Singapore.
6. **Li, H.F., Foo, Y.L. & Ramanujan, R.V.** (2005). In-situ TEM observations of the coarsening of a nanolamellar structure in a cobalt based magnetic alloy. *Journal of Materials Science*, 40, 1901-1907.
7. **Li, H.F., Ramanujan, R.V. & Laughlin, D.E.** (2005). Nanocrystallization of an $\text{Fe}_{44.5}\text{Co}_{44.5}\text{Zr}_7\text{B}_4$ amorphous magnetic alloy. *Philosophical Magazine*, accepted for publication.
8. **Li, H.F. & Ramanujan, R.V.** (2005). Synthesis of FeCo based nanomagnetic materials, special issue in *Trans IIM*, (invited), accepted for publication.

Manuscripts

1. **Li, H.F.**, Foo, Y.L. & Ramanujan, R. V. The Crystallography of A Nanolamellar Structure Formed by Crystallization of Amorphous Magnetic Alloy $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$. Submitted to *IEEE Transactions on Nanotechnology*.
2. **Li, H.F.**, Foo, Y.L. & Ramanujan, R.V. In-situ TEM observations of the crystallization of a cobalt based $\text{Co}_{65}\text{Si}_{15}\text{B}_{14}\text{Fe}_4\text{Ni}_2$ amorphous magnetic alloy, submitted to *Thin Solid Film*.