Direct Synthesis of $L1_0$ ($\text{Fe}_{0.55}\text{Pt}_{0.45}$) $_{77-78}\text{Zr}_{2-5}\text{B}_{17-20}$ Nanocrystalline Alloys with High Coercivity by Melt-Spinning

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The structure and the coercivity (H_c) of the rapidly quenched ($\text{Fe}_{0.55}\text{Pt}_{0.45}$) $_{\text{bal.}}$ $\text{Zr}_{0-8}\text{B}_{0-24}$ alloys prepared by the melt-spinning technique have been investigated. The ordered $L1_0$ -FePt phase with a size of 20–200 nm was directly formed by rapidly quenching the melt in the compositional range of 2–5 at% Zr and 17–20 at% B, and the alloys exhibit H_c greater than 200 kA/m in an as-quenched state. In particular, the melt-spun ($\text{Fe}_{0.55}\text{Pt}_{0.45}$) $_{78}\text{Zr}_2\text{B}_{20}$ and ($\text{Fe}_{0.55}\text{Pt}_{0.45}$) $_{78}\text{Zr}_4\text{B}_{18}$ alloys exhibit high H_c of 341 kA/m and 649 kA/m, respectively. The melting temperature (T_m) remarkably decreases by the addition of Zr and B, e.g., from 1833 K for $\text{Fe}_{55}\text{Pt}_{45}$ to 1360 K for ($\text{Fe}_{0.55}\text{Pt}_{0.45}$) $_{78}\text{Zr}_4\text{B}_{18}$. The $L1_0$ phase, which is directly formed by the rapidly quenching method, is considered to include Zr and B, shows high thermal stability and maintains up to T_m . On the other hand, the ($\text{Fe}_{0.55}\text{Pt}_{0.45}$) $_{77-85}\text{Zr}_{0-8}\text{B}_{15-22}$ alloys, produced by the Cu-mold casting with a lower cooling rate than the melt-spinning technique are found to comprise of mixed structures of $L1_0$ -FePt and some compound phases such as ZrB_{12} , PtZr, Fe_3B , and FeB, and the alloys have a H_c of 40–100 kA/m, which is lower than that of the melt-spun alloys. Apart from the $L1_0$ phase, the other phases such as ZrB_{12} , PtZr, Fe_3B , and FeB are suppressed and the $L1_0$ phase containing Zr and B elements is formed by rapidly quenching the alloy melt with low T_m . The simultaneous addition of Zr and B facilitates the direct formation of the ordered $L1_0$ phase with a grain size of 20–200 nm by rapidly quenching the melt through the effect of the decreasing T_m and the increasing the stability of the $L1_0$ phase by the solution of Zr and B into the phase.

(Received May 26, 2004; Accepted July 7, 2004)

Keywords: iron-platinum alloy, ordered $L1_0$ phase, melt-spinning technique

1. Introduction

The $L1_0$ family of ferromagnets includes the intermetallic phases FePt, CoPt, FePd and MnAl which form stable or metastable phases in the vicinity of the equiatomic compositions. The tetragonal $L1_0$ phases are characterized by a high uniaxial magnetocrystalline anisotropy ($7 \times 10^6 \text{ J/m}^3$ for FePt)¹⁾ along the easy c -axis.

The ordered $L1_0$ FePt alloy has long been anticipated as materials for permanent magnets because of their high magnetic anisotropy, high coercivity (H_c), and good corrosion resistance. Generally, near equiatomic FePt cast alloys primarily have a single $L1_0$ phase. However, these alloys do not exhibit high magnetic hardness,²⁾ despite the fact that the highest magnetocrystalline anisotropy is expected at the equiatomic composition. Thus, a heat treatment is performed to achieve magnetic hardness. This involves heating at temperatures higher than the order-disorder transformation temperature (T_{tr}) and water-quenching for homogenizing to the fcc phase, followed by aging at temperatures lower than T_{tr} for transforming the fcc phase into the $L1_0$ phase. Even after the heat treatment, the equiatomic FePt alloy has an inferior magnetic hardness of 135 kA/m,²⁾ which is lower than that expected. High H_c of 340 kA/m was reported in an off-equiatomic bulk $\text{Fe}_{61.5}\text{Pt}_{38.5}$ alloy, which was homogenized to a fcc structure for 3.6 ks at 1598 K, higher than T_{tr} of 1360 K, quenched into ice water, and then aged for 360 ks at 773 K to form a mixed structure composed of the $L1_0$ and the fcc phases.²⁾ The high H_c is considered to originate from domain-wall pinning through the two phases.

The magnetic hardness of the $L1_0$ magnets is also strongly related to a defect structure comprised primarily of a high density of extended planar defects such as twins, antiphase

boundaries (APB), and stacking defects.^{3,4)} Zhang and Soffa proposed an APB pinning model to explain the changes in the magnetic hardness of the FePt alloys with the polytwinned microstructure conjugated along the $\{110\}$ planes.³⁾ Klemmer *et al.* reported that the enhanced H_c is achieved in the $L1_0$ FePd by a thermomechanical treatment that refines the grain size.⁴⁾ The grain size hardening is expected to be very small in coarse-grained, conventionally heat-treated materials (typically 20–30 μm), and in polytwinned structures. However, the grain size hardening is significant when the grain size approaches the single domain particle size, which is estimated to be 0.34 μm for FePt.⁴⁾ Since the order-disorder transformation temperature (T_{tr}) of the equiatomic FePt alloy is very high (about 1573 K),⁵⁾ the ordering process easily progresses during quenching from a temperature above T_{tr} because the atomic diffusion rate is rapid at such high temperatures. As a consequence of the rapid ordering process, a coarsening of the polytwinned structure and a reduction of the APB density also take place, and therefore, it is considered that high H_c cannot be obtained in a bulk equiatomic FePt alloy.

The FePt alloy is currently considered to be one of the most promising materials for ultrahigh density magnetic recording media due to its high magnetocrystalline anisotropy that is expected to realize the very small critical grain size for superparamagnetism.⁶⁾ Therefore, many studies on the thin films have been carried out by using the vapor-quenching method, such as the sputtering or evaporation techniques, with extremely high cooling rates.^{7–9)} However, the structure of the thin films and the melt-spun alloys^{10,11)} is generally a disordered fcc, which should be formed during the high cooling process,⁷⁾ because the equilibrium phase is a disordered fcc at a high temperature just below the melting temperature.

Therefore the rapidly quenching method from the melt or vapor might be effective for refining the structure, but not effective for the formation of the $L1_0$ structure. Heating a substrate during deposition and/or post-annealing for the thin films or the melt-spun alloys is necessary in order to obtain the $L1_0$ phase, and its temperature is generally above 773 K. However, such high-temperature treatment should cause grain growth, which results in a low H_c , and deteriorate the cheap glass substrates of the thin films. Therefore, it is vital to reduce the annealing temperature below 600 K, and attempts have been made to achieve this.^{9,12–16}

We have already known from the study on Fe-M-B (M = Zr, Hf, and Nb) soft magnetic nanocrystalline alloys^{17–20} that melting temperature (T_m) remarkably decreases for Fe by the simultaneous addition of Zr and B, e.g., the T_m of pure Fe is considerably decreased from 1811 K to about 1550 K by the addition of 7 at% Zr and 3 at% B, which results in the formation of an amorphous structure.^{17–19} Therefore, if T_m of the FePt alloys could be decreased by the addition of Zr and B, T_{tr} might decrease. Furthermore, it is reported that the annealing temperature for the ordering process of $L1_0$ -CoPt is significantly decreased by a small addition of B.^{15,16} Additionally, as the mixing enthalpy between Pt and Zr is known to be a large negative value of -100 kJ/(mole of atoms),²¹ some particular changes in the formation and thermal stability of the $L1_0$ phase are expected by using the rapidly quenching method on the melt.

In the present paper, the effect of addition of Zr and B on the melting temperature, the formation of the $L1_0$ phase, and the magnetic hardness of the melt-spun alloys is described.

2. Experimental Procedure

In this study, the ratio of Fe to Pt was fixed at 55:45 which is located center of the region where the $L1_0$ phase is formed.⁵ Alloy ingots, which are termed as the Cu-mold cast alloys in this paper, were prepared by arc melting and casting in a water-cooled Cu-mold in an Ar atmosphere. A single-roller melt-spinning method in an Ar atmosphere was used to produce rapidly solidified alloys. Ribbon samples with a width and thickness of about 1 mm and about 15 μ m, respectively, were obtained. The structure of the samples was examined by powder X-ray diffractometry (XRD) and transmission electron microscopy (TEM). The samples for TEM observation were prepared by ion-milling both sides of the ribbons. In order to examine the alloy structure at high temperatures, *in situ* high-speed XRD (scan time $\approx$ 240 s) was performed by using the semiconductor array detector. The powdered samples were heated to the measuring temperature at a heating rate of 0.17 K/s, and were maintained at the fixed temperature during the *in situ* XRD measurement. The room temperature magnetic properties were measured with the ribbon samples with a length of about 3 mm or small chips of the Cu-mold cast alloys by a vibrating sample magnetometer (VSM) with a maximum field (H_m) of 1 MA/m or a superconducting quantum interference device (SQUID) magnetometer with H_m of 4 MA/m. Thermal properties were examined by a differential scanning calorimeter (DSC) with a heating rate of 0.17 K/s up to 1623 K. Annealing treatment of the samples was carried out in a vacuum.

Fig. 1 Compositional dependence of coercivity (H_c) and structure of Cu-mold cast ($\text{Fe}_{0.55}\text{Pt}_{0.45}$)-Zr-B alloys.

3. Results and Discussion

The compositional dependence of H_c and the structure determined by XRD for the Cu-mold cast ($\text{Fe}_{0.55}\text{Pt}_{0.45}$)-Zr-B alloys is shown in Fig. 1. The maximum H_c was obtained for the binary $\text{Fe}_{55}\text{Pt}_{45}$ with a single $L1_0$ structure. The addition of Zr and/or B changes the alloy structure to one with some compound phases. The ($\text{Fe}_{0.55}\text{Pt}_{0.45}$)-B alloys are composed of $L1_0 + \text{Fe}_3\text{B} + \text{FeB}$, and H_c decreases with an increase in B content. For the ($\text{Fe}_{0.55}\text{Pt}_{0.45}$)-Zr_{4–8}B alloys with 10 at% B or less, the structure is composed of some compound phases, and H_c rapidly decreases with an increase in Zr content. However, by increasing B content above 15 at%, the $L1_0$ phase is formed. In the case of the Cu-mold casting with a relatively lower cooling rate, the addition of Zr and B is found to be non-effective for the formation of the $L1_0$ phase and improvement of magnetic hardness.

Figure 2 shows the compositional dependence of H_c and the structure for the melt-spun ($\text{Fe}_{0.55}\text{Pt}_{0.45}$)-Zr-B alloys in an as-quenched state. The mixed structure of a disordered fcc and an ordered $L1_0$ FePt phase is formed in the compositional range of 2–8 at% Zr and 15–24 at% B. The structure composed of the $L1_0$ phase with a minor segment of the fcc phase is formed in the compositional range of 2–5 at% Zr and 17–20 at% B where the H_c higher than 200 kA/m is obtained. Figures 3 and 4 show the XRD profiles and the TEM images of the melt-spun (a) ($\text{Fe}_{0.55}\text{Pt}_{0.45}$)₇₈Zr₂B₂₀ and (b) ($\text{Fe}_{0.55}$ -

Fig. 2 Compositional dependence of coercivity (H_c) and structure of melt-spun ($\text{Fe}_{0.55}\text{Pt}_{0.45}$)-Zr-B alloys in an as-quenched state.

Fig. 3 X-ray diffraction profiles of melt-spun (a) $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_2\text{B}_{20}$ and (b) $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloys in an as-quenched state.

Fig. 5 X-ray diffraction profiles of (a) Cu-mold cast and (b) melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloys.

Fig. 4 TEM images of melt-spun (a) $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_2\text{B}_{20}$ and (b) $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloys in an as-quenched state.

$\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloys. These results reveal that both the structures are mainly composed of the L1₀ grains with sizes of 20–100 nm for $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_2\text{B}_{20}$ and 40–200 nm for $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$, which might be smaller than the single domain size.⁴⁾ In the TEM images obtained, the bright and dark grains were observed. The brightness of the grains seems to reflect the difference in the composition and/or the diffraction condition of the grains. These alloys exhibit a high

H_c of 341 kA/m for $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_2\text{B}_{20}$ and 649 kA/m for $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ in an as-quenched state. The H_c of the $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloy is much higher than that of the annealed bulk $\text{Fe}_{61.5}\text{Pt}_{38.5}$ (Ref. 2) and the melt-spun $(\text{Fe}_{0.65}\text{Pt}_{0.35})_{83}\text{B}_{17}$ (Ref. 11) alloys already reported. In the case of the Fe-rich Fe-Zr-B system, we have already reported that an amorphous structure is formed in the wide compositional range except for the regions with Zr content higher than approximately 13 at% or with Zr content lower than approximately 6 at% and B content lower than approximately 8 at%;¹⁹⁾ however, the addition of a large amount of Pt to the Fe-Zr-B system drastically changes the as-quenched structure.

Figure 5 shows the comparison of the structure of the (a) Cu-mold cast and (b) the melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloys. As already described, the Cu-mold cast alloy has a mixed structure of L1₀-FePt, ZrB₁₂, PtZr, and Fe₃B phases, whereas the structure of the melt-spun alloy is mainly composed of the L1₀ phase without any compounds. The difference in the structure should result in a remarkable difference in H_c between the alloys; the melt-spun alloy exhibits high H_c of 649 kA/m, which is about 9 times as large as that of the Cu-mold cast alloy.

Figure 6 shows the magnetization curves of the Cu-mold cast $\text{Fe}_{55}\text{Pt}_{45}$ binary alloy and the melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloy in an as-quenched state. The melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloy exhibits H_c over 3 times as large as that of the Cu-mold cast $\text{Fe}_{55}\text{Pt}_{45}$ alloy. The estimated value of the remanence ratio is about 0.5–0.6 for both the alloys, which implies that the alloys are isotropic. The remarkable difference of H_c between the alloys might have resulted from the difference in some structural properties. Considering that both alloys have structures mainly composed of the L1₀ phase, one of the reasons should be the difference in the grain size: 40–200 nm and 20–30 nm

Fig. 6 Magnetization curves of Cu-mold cast $\text{Fe}_{55}\text{Pt}_{45}$ binary alloy and melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloy in an as-quenched state.

Fig. 7 Annealing temperature dependence of coercivity of melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ and Cu-mold cast $\text{Fe}_{55}\text{Pt}_{45}$ alloys. t_a denotes the annealing time.

(Ref. 4) for the melt-spun and the Cu-mold cast alloys, respectively.

The annealing induced a change in H_c for both the alloys is shown in Fig. 7. The H_c of the melt-spun alloy with Zr and B increases, while that of the Cu-mold cast alloy considerably decreases by annealing. This result indicates that the $L1_0$ structure directly formed by the rapidly quenching method should not substantially change with annealing; the grain size of the melt-spun alloy may still be smaller than the single domain particle size after annealing. On the other hand, the structure of the Cu-mold cast alloy should undergo a change, most probable with regard to the grain growth and the reduction of some defects such as APB. Therefore, it can be said that the melt-spun $L1_0$ structure shown in Fig. 4 has a higher thermal stability than that of the Cu-mold cast $\text{Fe}_{55}\text{Pt}_{45}$ alloy despite the melt-spun $L1_0$ being is the non-equilibrium phase.

Table 1 shows the lattice parameters and the axial ratio at room temperature of the $L1_0$ and the fcc phases for the $\text{Fe}_{55}\text{Pt}_{45}$ binary alloy produced by the Cu-mold casting²²⁾ and the melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_2\text{B}_{20}$ and $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloys in an as-quenched state. The minor lattice parameter (c_{fct}) of the $L1_0$ phase for both the melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_2\text{B}_{20}$ and $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloys is 0.372 ± 0.001 nm, which is equal to that of the Cu-mold cast $\text{Fe}_{55}\text{Pt}_{45}$ binary alloy whose $L1_0$ phase should be almost perfectly ordered.²²⁾ On the other hand, the major lattice parameter (a_{fct}) of the $L1_0$ phase for the $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_2\text{B}_{20}$ and $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloys are slightly larger than that of the $\text{Fe}_{55}\text{Pt}_{45}$ alloy ($a_{\text{fct}} = 0.383 \pm 0.001$ nm). Furthermore, comparison between $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_2\text{B}_{20}$ and $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloys indicate that the a_{fct} and the lattice parameter of the minority fcc phase (a_{fcc}) both increase with an increase in Zr content, which has the largest atomic radius among the constituent elements.²³⁾ Thus, considering the fact that it is unknown which interstitial or substitutional site in the lattice should be occupied by B atoms, it is acceptable to consider that Zr and B elements are contained in the $L1_0$ and the fcc phases, which might be closely related to the high thermal-stability of the melt-spun $L1_0$ structure.

Next, the effect of independent addition of Zr or B is discussed. Figure 8 shows the XRD profiles for ternary

Fig. 8 X-ray diffraction profiles of melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{92}\text{Zr}_8$ alloy (a) in an as-quenched state and (b) after annealing at 923 K for 1.8 ks.

Table 1 Lattice parameters (a and c) and axial ratio (c/a) at room temperature of $L1_0$ (fct) and fcc phases for $\text{Fe}_{55}\text{Pt}_{45}$ binary alloy produced by Cu-mold casting²²⁾ and melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_2\text{B}_{20}$ and $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloys in an as-quenched state.

	$L1_0$			fcc
	a_{fct} (nm)	c_{fct} (nm)	$c_{\text{fct}}/a_{\text{fct}}$	a_{fcc} (nm)
$\text{Fe}_{55}\text{Pt}_{45}$	0.383 ± 0.001	0.372 ± 0.001	0.971 ± 0.004	—
$(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_2\text{B}_{20}$	0.385 ± 0.001	0.372 ± 0.001	0.966 ± 0.004	0.392 ± 0.003
$(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$	0.387 ± 0.001	0.372 ± 0.001	0.961 ± 0.004	0.396 ± 0.001

Fig. 9 X-ray diffraction profiles of melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{85}\text{B}_{15}$ alloy (a) in an as-quenched state and (b) after annealing at 923 K for 1.8 ks.

$(\text{Fe}_{0.55}\text{Pt}_{0.45})_{92}\text{Zr}_8$ in an as-quenched state and after annealing at 923 K for 1.8 ks. The alloy has a mixed structure composed of some compounds such as Fe_3Zr , Fe_2Zr , and Pt_3Zr_5 . Even after annealing, the $L1_0$ phase is not found and H_c is low. As shown in Fig. 9, the ternary $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{85}\text{B}_{15}$ alloy without Zr has a structure with the major part being an fcc phase without any compounds in an as-quenched state. The fcc phase changes to the $L1_0$ phase by annealing at 923 K for 1.8 ks, and H_c increases from 25 kA/m to 357 kA/m. This result is almost in agreement with that already reported.¹¹⁾ These results reveal that the direct synthesis of the $L1_0$ structure by melt-spinning can be realized only by the simultaneous addition of Zr and B.

The DSC curves obtained for the melt-spun alloys can be classified into two types, which are characterized by two distinct endothermic peaks or one endothermic peak. Figure 10(a) shows the DSC curves of the melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{77}\text{Zr}_8\text{B}_{15}$ alloy. The two endothermic peaks approximately at 1336 K and 1406 K are found for $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{77}\text{Zr}_8\text{B}_{15}$. The endothermic reaction of the high temperature side corresponds to the melting because no endothermic reaction was observed above 1500 K and the sample had completely melted after the DSC measurement. The origin of the endothermic peak observed at the lower temperature, approximately 1336 K, was studied. Figures 10(b)–(d) show the XRD profiles of the melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{77}\text{Zr}_8\text{B}_{15}$ alloy at room temperature and at high temperatures. The sample was first heated to 1298 K and subsequently heated to 1373 K. The heating rate was 0.17 K/s which is the same value as that for the DSC measurements. The structure, which mainly comprised the fcc phase in an as-quenched state, changed into a mixed structure composed of the $L1_0$, the fcc, the FeZr_3 , and the PtB phases at 1298 K. Most of the fcc phase transforms

Fig. 10 (a) DSC curve and (b)–(d) *in situ* X-ray diffraction (XRD) profiles of melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{77}\text{Zr}_8\text{B}_{15}$ alloy measured at (b) 300 K, (c) 1298 K and (d) 1373 K. The upward arrows in Fig. (a) indicate the measuring temperature of the XRD profiles. The peak marked by $\times$ in Figs. (b)–(d) derives from the sample holder.

into the $L1_0$ phase during heating. The $L1_0$ phase is stable up to 1298 K, which is slightly lower than that at 1336 K at which the endothermic reaction takes place. On the other hand, the XRD profile measured at 1373 K, which is a temperature between the two endothermic reactions, shows that the alloy is mainly constituted by the fcc phase. Therefore it can be said that the endothermic reaction at the low temperature side originates from the order-disorder transformation of the FePt phase. Thus, the structural change in the alloy with an increase in temperature can be illustrated as shown in the upper part of Fig. 10. Figure 11 shows (a) the DSC curve for the melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloy and (b)–(d) the XRD profiles of the alloy at room temperature and at high temperatures, which are measured by the same condition as that of the $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{77}\text{Zr}_8\text{B}_{15}$ alloy shown in Figs. 10(b)–(d). The DSC curve has one large endothermic peak or two peaks overlapping each other. A comparison of the XRD profiles reveals that the volume fraction of the fcc phase grows smaller with an increase in temperature and

Fig. 11 (a) DSC curve and (b)–(d) *in situ* X-ray diffraction (XRD) profiles of melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloy measured at (b) 300 K, (c) 1223 K and (d) 1353 K. The upward arrows in Fig. (a) indicate the measuring temperature of the XRD profiles. The peak marked by $\times$ in Figs. (b)–(d) derives from the sample holder.

disappears at 1353 K, which is almost equal to the onset temperature of the endothermic peak. With a further increase in temperature, the alloy sample partially melts at 1373 K. These results suggest that the endothermic peak corresponds to the melting and the order-disorder transformation does not take place below T_m . Therefore, the results of DSC and XRD enable us to determine the phase change with increasing temperatures, which is illustrated in Fig. 11.

The compositional dependence of T_m , which is determined from the onset temperature of the endothermic peak, of the melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})\text{-Zr-B}$ alloys is shown in Fig. 12. With an increase in B content, T_m drastically decreases. The low T_m region, *i.e.*, below 1370 K, is 0–4 at% Zr and 18–24 at% B, and the lowest T_m is 1360 K for $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$. This T_m is as much as 473 K lower than 1833 K of $\text{Fe}_{55}\text{Pt}_{45}$, and also lower than T_{tr} at 1548 K for the binary alloy. This is mainly for the eutectic reaction of Pt and B; *i.e.*, a $\text{Pt}_{66.1}\text{B}_{33.9}$ alloy, which has the same compositional ratio of the $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$ alloy, exhibits a low T_m of 1163 K and a low liquidus temperature of approximately 1183 K.⁵⁾

Fig. 12 Compositional dependence of melting temperature (T_m) of melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})\text{-Zr-B}$ alloys. T_m for $\text{Fe}_{55}\text{Pt}_{45}$ binary alloy is quoted from Ref. 5.

Fig. 13 Compositional dependence of temperature interval between melting temperature (T_m) and order-disorder transformation temperature (T_{tr}) of melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})\text{-Zr-B}$ alloys. The value for $\text{Fe}_{55}\text{Pt}_{45}$ binary alloy is quoted from Ref. 5.

By comparing the compositional dependence of the structure, H_c (Fig. 2) and T_m (Fig. 12), we notice that the compositional range in which the $L1_0$ phase is directly formed and a high H_c is obtained is coincident with that where low T_m is observed, and the highest H_c and the lowest T_m is obtained for $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$. Thus, it can be said that the direct formation of the $L1_0$ phase and high H_c in an as-quenched state are closely related to low T_m for the melt-spun alloys. Figure 13 shows the compositional dependence of the temperature interval between T_m and T_{tr} in the DSC curve for the melt-spun $(\text{Fe}_{0.55}\text{Pt}_{0.45})\text{-Zr-B}$ alloys, which implies the temperature range in which the fcc phase is stable. Judging from Figs. 12 and 13, it appears that the $L1_0$ phase is stabilized by the addition of 2–6 at% Zr. In the compositional range, indicated by the gray color in Fig. 13, the order-disorder transformation was not observed in the DSC curve, where the melt-spun $L1_0$ phase is stable up to T_m . This compositional range is found to be almost in agreement with that in which T_m is lower than approximately 1400 K. Therefore, in this compositional region, the ordered $L1_0$ phase should be directly synthesized without forming the disordered fcc phase during the rapid solidification.

4. Conclusions

- (1) The addition of Zr and B remarkably decreases the melting temperature.
- (2) The lowest melting temperature is 1360 K for $(\text{Fe}_{0.55}\text{Pt}_{0.45})_{78}\text{Zr}_4\text{B}_{18}$, which is much lower than 1833 K of $\text{Fe}_{55}\text{Pt}_{45}$.

(3) The melt-spun L1₀ structure changes to melt without undergoing the order-disorder transformation by heating in the compositional range in which T_m is lower than approximately 1400 K.

(4) The L1₀ structure can be directly synthesized by rapidly quenching the melt in the compositional region of 2–5 at% Zr and 17–20 at% B, where T_m is lower than 1370 K without forming the fcc phase.

(5) The low melting temperature that resulted from the addition of Zr and B appears to facilitate the formation of the ordered L1₀ phase during the rapidly quenching method of the alloy melt.

(6) The melt-spun (Fe_{0.55}Pt_{0.45})₇₈Zr₂B₂₀ and (Fe_{0.55}Pt_{0.45})₇₈Zr₄B₁₈ alloys with the L1₀ structure exhibit the high H_c of 341 kA/m and 649 kA/m, respectively in an as-quenched state. Furthermore, these alloys have a high thermal stability.

Acknowledgements

This work was entrusted with the “Nanohetero Metallic Materials” as a part of the Special Coordination Funds for Promoting Science and Technology from the National Institute Materials Science (NIMS). We wish to thank Associate Professor H. Amitsuka and Dr. K. Tenya of Hokkaido Univ. for their help in the magnetization measurements by the SQUID magnetometer.

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