The effect of annealing on the magnetic phase diagram for the Y-Fe amorphous alloy system

1994 J. Phys.: Condens. Matter 6 5741

(http://iopscience.iop.org/0953-8984/6/29/016)

J. Phys.: Condens. Matter 6 (1994) 5741–5750. Printed in the UK

The effect of annealing on the magnetic phase diagram for the Y–Fe amorphous alloy system

T Suzuki†, A Fujita†, K Fukamichi† and T Goto‡

† Department of Materials Science, Faculty of Engineering, Tohoku University, Sendai 980, Japan

‡ Institute for Solid State Physics, The University of Tokyo, Roppongi 106, Japan

Received 4 February 1994

Abstract. The annealing effect on the magnetic phase diagram of the Y–Fe amorphous alloy system has been investigated by means of differential magnetic susceptibility. Y–Fe amorphous alloys annealed at 250 °C for 30 min exhibit a re-entrant spin-glass behaviour in a similar manner to the as-prepared samples in an applied magnetic field. The Curie temperature is enhanced but the spin-freezing temperature T_f is depressed by annealing. These facts suggest that the Fe–Fe interatomic distance, which significantly influences the magnetic properties, increases on annealing. The magnetic phase diagram of the Y–Fe amorphous alloy system in an applied magnetic field is similar to that of various re-entrant spin-glass-type Fe-based amorphous alloy systems in zero magnetic field.

1. Introduction

Various Fe-based amorphous alloy systems RE–Fe (RE: rare earth metal) (Fukamichi *et al* 1989a) and ET–Fe (ET: early transition metal) (Fukamichi *et al* 1989b) exhibit a re-entrant spin-glass behaviour, namely, the magnetic state changes from a paramagnetic to a ferromagnetic state and finally re-enters a spin-glass state with decreasing temperature. On the other hand, the magnetic properties of Y–Fe amorphous alloys with 32–88% Fe were investigated by magnetization and Mössbauer-effect measurements (Coey *et al* 1981, Chappert *et al* 1981), and no ferromagnetic phase was observed in this concentration range. That is, this amorphous alloy system has only a spin-glass state at low temperatures. Therefore, this system is quite unique, compared with other Fe-based amorphous alloy systems mentioned above. Recently, however, it has been reported that Y–Fe amorphous alloys have a re-entrant spin-glass state at low temperatures in weak external magnetic fields (Fujita *et al* 1993). This fact suggests the magnetic state in Y–Fe amorphous alloys is very close to ferromagnetism.

Volume-dependent instabilities of the Fe moment have been discussed extensively from the experimental and theoretical viewpoints and the drastic change from the antiferromagnetic state with a small moment to the ferromagnetic state with a large moment occurs at around 2.5 Å for the Fe–Fe interatomic distance in FCC Fe (Wassermann 1990). The Fe–Fe interatomic distance for $Y_{33.3}Fe_{66.7}$ amorphous alloy has been estimated to be 2.54 Å (Forester *et al* 1979). Moreover, it has been reported that the Fe–Fe interatomic distance in Fe-based amorphous alloys is very close to 2.5 Å (Matsuura *et al* 1989). It is well known that annealing of amorphous alloys brings about structural relaxation due to rearrangement of atoms. Accordingly, it is expected that the magnetic properties of Fe-based

0953-8984/94/295741+10$19.50

amorphous alloys are significantly influenced by even a slight change in the environment, such as the Fe–Fe interatomic distance, on annealing.

Magnetization (M) is one of the order parameters that show the magnetic state of materials, and a paramagnetic state has no spontaneous magnetization ($M = 0$), whereas a ferromagnetic state does ($M \neq 0$). In a spin-glass state, there is competition between positive and negative interactions such that M becomes zero. Therefore, the differential magnetic susceptibility is theoretically divergent and experimentally shows a cusp at the transition temperature. Although no spontaneous magnetization is observed in either the paramagnetic or spin-glass states, the differential magnetic susceptibility shows a peak at the spin-freezing temperature. Another order parameter (Q) (Edwards and Anderson 1975) which represents the time dependence of the direction of each spin, changes from a certain positive value in the spin-glass state to zero in the paramagnetic state. The free energy as a function of the order parameters M and Q has been obtained (Sherrington and Krikpatrick 1975), and the differential magnetic susceptibility $\mathrm{d}M/\mathrm{d}H$ was calculated by differentiating with respect to the magnetic field H, and the relation between $\mathrm{d}M/\mathrm{d}H$ and $\mathrm{d}Q/\mathrm{d}H$ was obtained (Nieuwenhuys *et al* 1978). According to these calculations, the temperature variations of M and Q reflect that of the differential magnetic susceptibility $\mathrm{d}M/\mathrm{d}H$. Therefore, the measurement of the differential magnetic susceptibility is valuable in determining the phase transition temperatures, e.g. the Curie and spin-freezing temperatures. In the present paper, the effect of annealing on the magnetic phase diagram of the Y–Fe amorphous alloy system is investigated by means of differential magnetic susceptibility, the magnetic cooling effect and AC magnetic susceptibility measurements.

2. Experimental details

$Y_{100-x}Fe_x$ amorphous alloys ($x = 92.5$, 90, 84, 80 and 70) were prepared by a high-rate DC sputtering technique on a Cu substrate using alloy targets made by arc melting in an Ar atmosphere. The size of the alloy target was about 40 mm in diameter. The Ar gas pressure during sputtering was 40 mTorr, and the target voltage and anode current were 1.0 kV and 6.0 A, respectively. The sputtering was carried out continuously for about 2.5 days in order to obtain samples of thickness about 0.2 mm. The Cu substrate was dissolved in a solvent, CrO_3 (500 g) + H_2SO_4 (27 cm^3) + H_2O (1000 cm^3), at a temperature of 350 K. The specimens were annealed *in vacuo* at 250 °C for 30 min. The structures of the samples before and after annealing were confirmed by x-ray diffraction. The measurements of differential magnetic susceptibility at various magnetic field strengths and the magnetic cooling effect at 200 Oe were carried out with a SQUID magnetometer. The AC magnetic susceptibility was measured at 1 Oe and 80 Hz from 4.2 K to 300 K.

3. Results and discussion

Since the crystallization temperature of $Y_{100-x}Fe_x$ amorphous alloys is in the range of about 850–970 K, being much higher than the annealing temperature (Fujita *et al* 1994), all annealed Y–Fe samples were confirmed to be amorphous by x-ray diffraction. Figure 1 shows the temperature dependence of the differential magnetic susceptibility for the $Y_{16}Fe_{84}$ amorphous alloy at various values of the magnetic field. The first peak and the second peak (or shoulder) are observed around 40 K and approximately 80–100 K, respectively, for magnetic fields up to 200 Oe. A third peak emerges around 180 K above 200 Oe. These peaks and shoulder are considered to be magnetic phase transition temperatures. Figures 2 and 3 show the results for annealed $Y_{20}Fe_{80}$ and $Y_{10}Fe_{90}$ amorphous alloys, respectively. The third peak appears in the $Y_{20}Fe_{80}$ amorphous alloy even at 100 Oe, but only one peak and a shoulder are observed for the $Y_{10}Fe_{90}$ amorphous alloy. According to the GT model (Gabay and Toulouse 1981), an isotropic spin glass exhibits a spin freezing of the transverse component (T_g) in a higher temperature range and of the longitudinal component (T_f) in a lower temperature range in an external magnetic field. Therefore, it is considered that the first peak and second peak (or shoulder) correspond to the spin-freezing temperatures T_f and T_g, respectively, for the annealed $Y_{20}Fe_{80}$, $Y_{16}Fe_{84}$ and $Y_{10}Fe_{90}$ amorphous alloys.

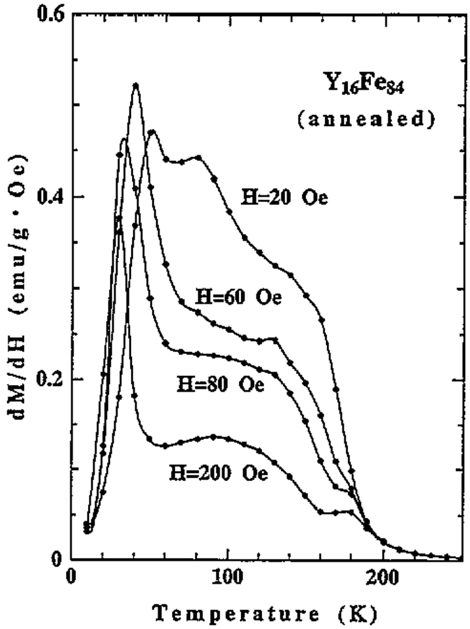

Figure 1. The temperature dependence of the differential magnetic susceptibility $\mathrm{d}M/\mathrm{d}H$ measured at 20, 60, 80 and 200 Oe for the annealed $Y_{16}Fe_{84}$ amorphous alloy.

The magnetic cooling effect in a field of strength 200 Oe for the annealed $Y_{20}Fe_{80}$, $Y_{16}Fe_{84}$ and $Y_{10}Fe_{90}$ amorphous alloys is shown in figure 4. In this figure, open and closed symbols represent the magnetization curves for alloys cooled in zero field and at 200 Oe, respectively. These curves show a clear magnetic hysteresis between zero-field-cooled (ZFC) and field-cooled (FC) processes, which shows the spin-glass behaviour. The arrows denote T_C, T_g and T_f obtained from figures 1–3. The former two samples exhibit re-entrant spin-glass behaviour, being accompanied by a very broad peak. The curves for the $Y_{10}Fe_{90}$ amorphous alloy also exhibit a broad peak. However, as seen from figure 5, AC magnetic susceptibility measurements in an extremely weak magnetic field of about 1 Oe exhibit a clear cusp at 105 K. These facts suggest that the magnetic state in the annealed $Y_{10}Fe_{90}$ amorphous alloy around 105 K is very close to the triple point of magnetic states, i.e. paramagnetic, ferromagnetic and spin-glass states.

The relation between the magnetic phase transition temperatures and the magnetic field for the annealed $Y_{16}Fe_{84}$ amorphous alloy is shown in figure 6, together with that for the as-prepared sample of the same composition for comparison. The results for the former

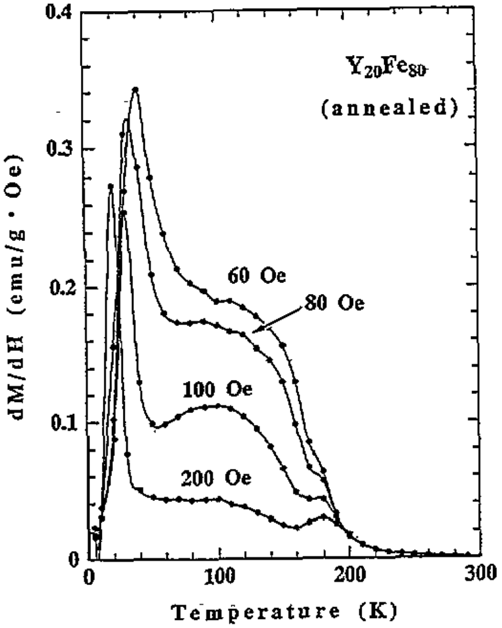

Figure 2. The temperature dependence of the differential magnetic susceptibility dM/dH measured at 60, 80, 100 and 200 Oe for the annealed $Y_{20}Fe_{80}$ amorphous alloy.

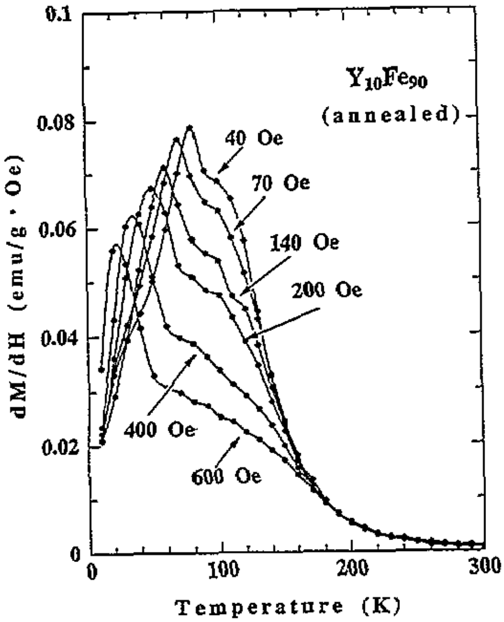

Figure 3. The temperature dependence of the differential magnetic susceptibility dM/dH measured at 40, 70, 140, 200, 400 and 600 Oe for the annealed $Y_{10}Fe_{90}$ amorphous alloy.

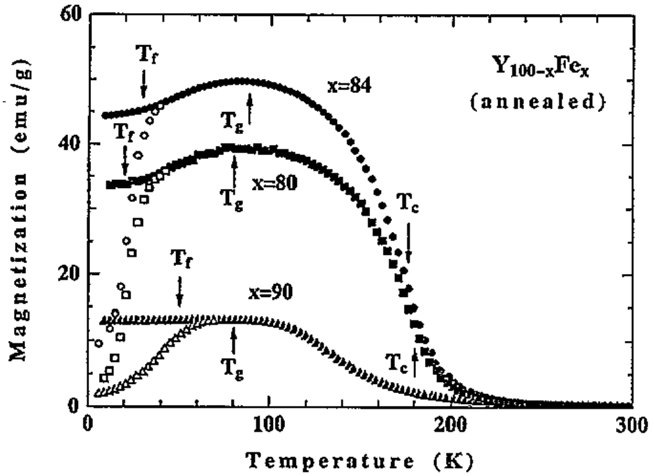

Figure 4. The magnetic cooling effect at 200 Oe for annealed $Y_{100-x}Fe_x$ ($x = 80$, 84 and 90) amorphous alloys. Open and closed symbols stand for the magnetization on cooling in zero field and at 200 Oe, respectively. The longitudinal and transverse spin-freezing temperatures are indicated by T_f and T_g, respectively, and T_C is the Curie temperature obtained from figures 1–3.

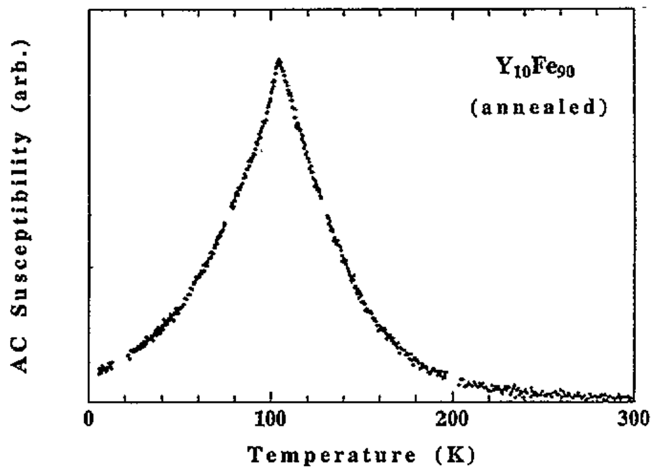

Figure 5. The temperature dependence of the AC magnetic susceptibility for the annealed $Y_{10}Fe_{90}$ amorphous alloy.

and the latter are given by the solid and dashed lines, respectively. In contrast with the Curie temperature T_C, the magnetic field dependence of the spin-freezing temperature T_f is significant. This pronounced magnetic-field dependence of T_f is caused by weakening of spin freezing in external magnetic fields. The shifts of the transition temperatures by annealing are clearly confirmed. That is, the spin-freezing temperature T_f becomes lower than that for the as-prepared sample by about 10 K, while the Curie temperature T_C shifts to higher temperature by about 40 K. This is because the ferromagnetic state is stabilized by annealing. On the other hand, the transverse spin-freezing temperature T_g is scarcely affected by annealing, though the field dependence is different for the two samples. The

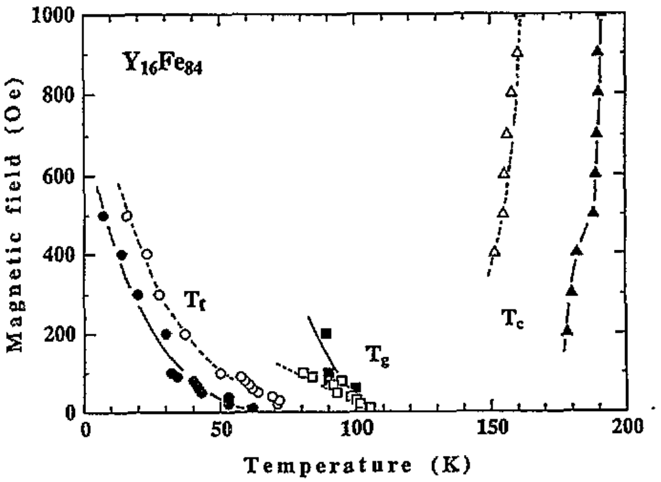

Figure 6. The magnetic-field dependence of the phase transition temperatures T_f, T_g and T_C for the annealed $Y_{16}Fe_{84}$ amorphous alloy. The solid lines with closed symbols and the dashed lines with open symbols denote the results for annealed and for as-prepared samples (Fujita *et al* 1993), respectively.

freezing temperatures T_f and T_g decrease with increasing strength of the applied field in accordance with the GT model (Gabay and Toulouse 1981).

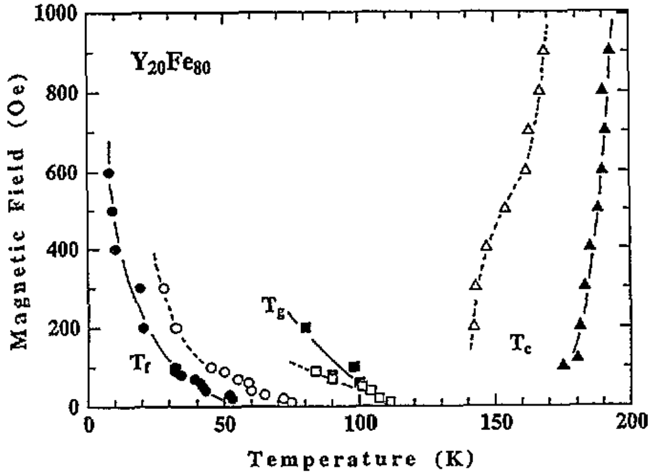

Figure 7. The magnetic-field dependence of the phase transition temperatures T_f, T_g and T_C for the annealed $Y_{20}Fe_{80}$ amorphous alloy. The solid lines with closed symbols and the dashed lines with open symbols denote the results for the annealed and for as-prepared samples (Fujita *et al* 1993), respectively.

In order to obtain a more complete and detailed picture, we have obtained similar plots for other annealed amorphous alloys. In figures 7 and 8 representative results for $Y_{20}Fe_{80}$ and $Y_{10}Fe_{90}$, respectively, are given by the solid lines, together with the results given

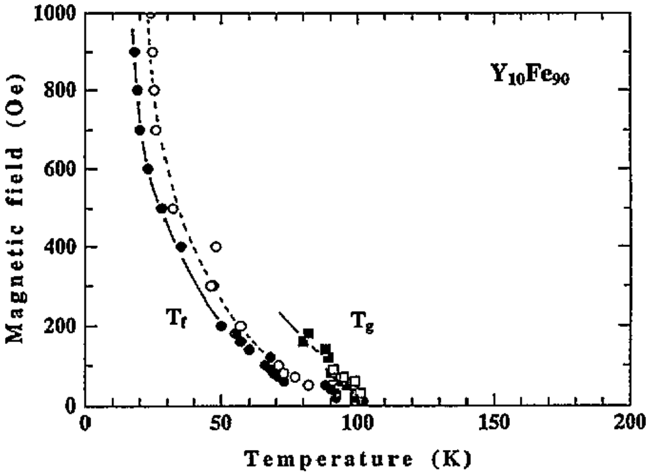

Figure 8. The magnetic-field dependence of the phase transition temperatures T_f and T_g for the annealed $Y_{10}Fe_{90}$ amorphous alloy. The solid lines with closed symbols and the broken lines with open symbols denote the results for annealed and for as-prepared samples (Fujita *et al* 1993), respectively.

by the dashed lines for the as-prepared samples (Fujita *et al* 1993). As seen from these figures, the trend of the magnetic field dependence of the phase transition temperatures is analogous to that for the annealed $Y_{16}Fe_{84}$ amorphous sample. That is, the longitudinal spin-freezing temperature T_f is decreased but the transverse spin-freezing temperature T_g is hardly influenced by annealing. From figures 6 and 7 it should be noted that the Curie temperature T_C appears just before or after smearing out of T_g. This means that short-range ferromagnetic clusters grow rapidly with increasing applied magnetic field. On the other hand, the Curie temperature is not confirmed for the annealed $Y_{10}Fe_{90}$ amorphous alloy in figure 8 and the spin-glass phase transition temperatures T_f and T_g come close to 105 K when the magnetic field is extrapolated to 0 Oe. This result is in good agreement with the AC susceptibility measurement shown in figure 5.

Figure 9 shows the magnetic phase diagram in a magnetic field of 500 Oe for the annealed Y–Fe amorphous system (solid lines), together with that for the as-prepared alloys in the same magnetic field (dashed lines) (Fujita *et al* 1993) and that for samples in zero magnetic field (dashed–dotted lines) (Komatsu and Fukamichi 1994) for comparison. The annealed Y–Fe amorphous system exhibits re-entrant spin-glass behaviour in a similar manner to the as-prepared samples in 500 Oe, but is very different from the diagram for zero magnetic field for the as-prepared samples. The re-entrant spin-glass behaviour in zero magnetic fields has been observed in many Fe-based amorphous alloys (Fukamichi *et al* 1989a, b). From this magnetic phase diagram, it is clear that the ferromagnetism is stabilized by an applied magnetic field for the as-prepared state and is further enhanced by annealing, whereas the freezing temperature T_f is decreased and further suppressed by the same procedures. As is well known, the magnetic properties of Fe-based alloys are sensitive to changes in the environment such as the Fe–Fe interatomic distance and the coordination number. It has been pointed out for various RE–Fe amorphous alloys that annealing brings about an increase in the Fe–Fe interatomic distance, resulting in an increase in the Curie temperature T_C and in a decrease in the freezing temperature T_f (Chiang *et al* 1994). The relation between the spin-freezing temperature and the fluctuation of atomic configuration,

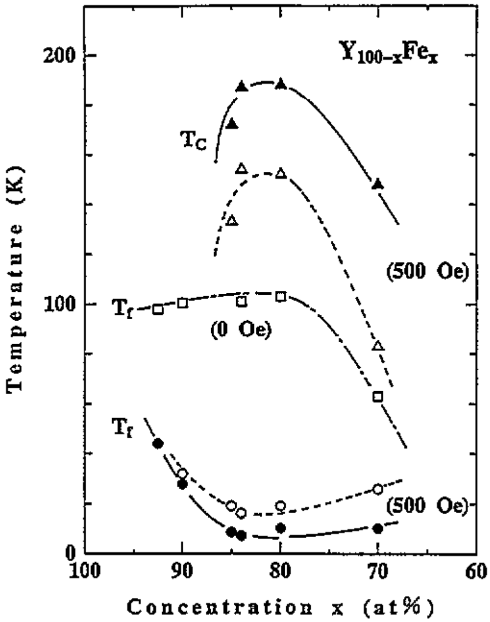

Figure 9. The magnetic phase diagram for the annealed Y–Fe amorphous alloy system in a magnetic field of 500 Oe, together with those for the as-prepared samples in the same magnetic field and in zero magnetic field. The solid lines with closed symbols and the dashed lines with open symbols denote the results for annealed and for as-prepared samples (Fujita *et al* 1993), respectively. The dashed–dotted line with square symbols indicates the results for the as-prepared Y–Fe amorphous alloy system in zero magnetic field (Komatsu and Fukamichi 1994).

i.e. the ratio of the mean interatomic distance and the deviation from it, has been calculated for amorphous Fe (Kakehashi 1990). According to this theory, taking into account the local environment effect, the spin-glass state of amorphous Fe is caused by the structural disorder, spin fluctuation and so on. This theory gives the result that the spin-freezing temperature becomes lower with decreasing fluctuation of atomic configuration. When the fluctuation of atomic configuration becomes smaller, the Fe–Fe ferromagnetic interaction becomes stronger. This leads to a decrease in the competition between ferromagnetic and antiferromagnetic interactions, that is, the spin-freezing temperature shifts to a lower temperature. The Y–Fe amorphous alloy system has been examined extensively, but its magnetic properties are unusually sensitive to the method and conditions of preparation. For example, evaporated amorphous films (Heiman and Kazama 1979) and sputtered amorphous alloys (Forester *et al* 1979, Coey *et al* 1981) exhibit spin-glass behaviour, but melt-spun $Y_{33.3}Fe_{66.7}$ has been reported to be ferromagnetic (Croat and Herbst 1982). It is interesting to note that the re-entrant spin-glass behaviour has been confirmed very recently without any annealing for melt-spun Y–Fe amorphous alloys over a wide composition range (Tange 1994).

The fluctuation of atomic configuration and the Fe–Fe interatomic distance of RE–Fe amorphous alloys can be observed using x-ray diffraction (Matsuura *et al* 1989). The anomalous x-ray scattering (AXS) method (Waseda *et al* 1988, Matsubara and Waseda 1992) in combination with the ordinary x-ray diffraction method would give more detailed information for the Y–Fe amorphous alloy system. Small-angle neutron scattering from the $Y_{33.3}Fe_{66.7}$ amorphous alloy indicates that there are only short-range ferromagnetic correlations below the freezing temperature and it exhibits dynamic behaviour (Pickart *et al* 1974, Murani and Rebouillat 1982) similar to that for a concentrated CuMn crystalline spin glass (Murani and Heideman 1978). Fe-based amorphous alloys (Fukamichi 1983, Fukamichi *et al* 1989a) and Fe-based crystalline FCC alloys (Wassermann 1990) exhibit a large spontaneous volume magnetostriction, which is mainly induced below the Curie temperature. On the other hand, Y–Fe amorphous alloys are not ferromagnetic in the as-prepared state, but they also exhibit a comparably large magnetovolume effect up to about 450 K, which is much higher than the spin-freezing temperature (Suzuki *et al* 1994). The inverse magnetic susceptibility shows anomalous behaviour in the same temperature range (Fujita *et al* 1994). Therefore, the microscopic magnetic structure in these amorphous alloys should be investigated in order to explain such a peculiar phenomenon. In the present study, the spin-glass state in the Y–Fe amorphous alloy system has been discussed on the basis of the coexistence of the spin-glass state and of the ferromagnetic ordering as per the GT model (Gabay and Toulouse 1981). On the other hand, the spin-glass behaviour of amorphous Fe is explained in terms of the frustration between the ferromagnetic interaction of the nearest-neighbour Fe–Fe pairs and the antiferromagnetic interaction of Fe–Fe pairs beyond the next-nearest neighbour (Kakehashi 1991). In order to investigate the spin-glass state, it is appropriate to examine the samples by means of neutron depolarization measurements. Indeed, $Fe_{19}Au_{81}$ and $Fe_{70}Al_{30}$ crystalline alloys, which are typical re-entrant spin glasses, have been studied using such measurements (Mitsuda *et al* 1992), and it has been pointed out that the magnetic state on a mesoscopic scale is quite different for these two alloys before and after entering the re-entrant spin-glass state. This method should, therefore, distinguish between spin-glass and ferromagnetic states in the Y–Fe amorphous alloy system. Both AXS and neutron depolarization experiments will be carried out in the near future.

4. Conclusions

$Y_{100-x}Fe_x$ amorphous alloys ($x = 92.5$, 90, 84, 80 and 70), prepared by DC high-rate sputtering, were annealed at 250 °C for 30 min and the magnetic phase diagram in a magnetic field investigated by differential magnetic susceptibility, the magnetic cooling effect and AC susceptibility. The main results are summarized as follows:

(i) annealed Y–Fe amorphous alloys, except for $Y_{7.5}Fe_{92.5}$ and $Y_{10}Fe_{90}$, exhibit re-entrant spin-glass behaviour in a magnetic field, in a similar manner to the as-prepared samples;

(ii) the Curie temperature T_C is enhanced but the spin-freezing temperature T_f is depressed by annealing;

(iii) with increasing applied magnetic field, the Curie temperature T_C appears just before or after smearing out the transverse spin-freezing temperature T_g;

(iv) the magnetic state in the annealed $Y_{10}Fe_{90}$ amorphous alloy around 105 K is considered to be very close to the triple point; and

(v) the magnetic phase diagram for the annealed Y–Fe amorphous alloy system in an external magnetic field is analogous to that for various Fe-based amorphous alloy systems that exhibit re-entrant spin-glass behaviour in zero magnetic field.

Acknowledgments

Grateful acknowledgment is made to Dr H Komatsu and Dr T H Chiang for preparation of the Y–Fe amorphous alloys. The authors are grateful to Professor N Kataoka for his helpful discussion. The present work has been supported by a grant-in-aid for scientific research (A), No 04402045, from the Japanese Ministry of Education, Science and Culture.

References

Chappert J, Coey J M D, Liénard A and Rebauillat J P 1981 *J. Phys. F: Met. Phys.* **11** 2727–44
Chiang T H, Matsubara E, Waseda Y and Fukamichi K 1994 unpublished
Coey J M D, Givord D, Liénard A and Rebauillat J P 1981 *J. Phys. F: Met. Phys.* **11** 2707–25
Croat J J and Herbst J F 1982 *J. Appl. Phys.* **53** 2294–6
Edwards S F and Anderson P W 1975 *J. Phys. F: Met. Phys.* **5** 965–74
Forester D W, Koon N C and Schelleng J H and Rhyne J J 1979 *J. Appl. Phys.* **50** 7336–41
Fujita A, Komatsu H, Fukamichi K and Goto T 1993 *J. Phys.: Condens. Matter* **5** 3003–10
Fujita A, Suzuki T, Kataoka N and Fukamichi K 1994 *Phys. Rev.* B at press
Fukamichi K 1983 *Amorphous Metallic Alloys* ed F E Luborsky (London: Butterworths) p 317
Fukamichi K, Goto T, Komatsu H and Wakabayashi H 1989a *Proc. 4th Int. Conf. on Physics of Magnetic Materials (Szczyrk-Biła, 1988)* ed H K Lachowicz and H Szymczak (Singapore: World Scientific) pp 354–80
Fukamichi K, Komatsu H, Goto T, Wakabayashi H and Matsuura M 1989b *Proc. MRS Int. Meeting on Advanced Materials (Tokyo, 1988)* vol 11, ed M Doyama *et al* (Pittsburg, PA: MRS) pp 285–99
Gabay M and Toulouse G 1981 *Phys. Rev. Lett.* **47** 201–4
Heiman N and Kazama N 1979 *Phys. Rev.* B **19** 201–32
Kakehashi Y 1990 *Phys. Rev.* B **41** 9207–22
—— 1991 *Phys. Rev.* B **42** 10 820–31
Komatsu H and Fukamichi K 1994 unpublished
Matsubara E and Waseda Y 1992 *Sci. Rep. RITU* A **36** 187–99
Matsuura M, Wakabayashi H, Goto T, Komatsu H and Fukamichi K 1989 *J. Phys.: Condens. Matter* **1** 2077–86
Mitsuda S, Yoshizawa H and Endoh Y 1992 *Phys. Rev.* B **45** 9788–97
Murani A P and Heideman A 1978 *Phys. Rev. Lett.* **41** 1402–6
Murani A P and Rebouillat J P 1982 *J. Phys. F: Met. Phys.* **12** 1427–37
Nieuwenhuys G J, Stocker H, Verbeek B H and Mydosh J A 1978 *Solid State Commun.* **18** 197–9
Pickart S J, Rhyne J J and Alperin H A 1974 *Phys. Rev. Lett.* **33** 424–7
Sherrington D and Kirkpatrick S 1975 *Phys. Rev. Lett.* **35** 1792–6
Suzuki T, Fujita A, Chiang T H and Fukamichi K 1994 *Mater. Sci. Eng.* at press
Tange H 1994 private communication
Waseda Y, Matsubara E and Sugiyama K 1988 *Sci. Rep. RITU* A **34** 1–14
Wassermann E F 1990 *Ferromagnetic Materials* vol 5, ed K H J Buschow and E P Wohlfarth (Amsterdam: North-Holland) p 237