The Curie Temperature of Magnetically Inhomogeneous Amorphous Fe-Zr-B Alloys

The Curie Temperature of Magnetically Inhomogeneous Amorphous Fe-Zr-B Alloys*

Hisao Kobayashi, Hideya Onodera, Hiroshi Yamauchi and Hisao Yamamoto

The Research Institute for Iron, Steel and Other Metals

(Received November 29, 1985)

Synopsis

The Curie temperature of amorphous Fe-Zr-B alloys was determined by both the Mössbauer thermal scan and a modified Arrott-plots methods. For amorphous $Fe_{92}(Zr_{1-x}B_x)_8$ alloys, the two methods make a difference between the values of T_C. On the other hand, for amorphous $Fe_{90}(Zr_{1-x}B_x)_{10}$ alloys, the results of the two methods agree with each other within limits of the experimental error. It is found that the magnetic inhomogeneity often causes the difficulty in the determination of T_C and the measurement of T_C necessitating external fields is accompanied by a serious problem in the case of the magnetically inhomogeneous materials. Since no external field is necessary, the Mössbauer thermal scan method is very useful for determining T_C of amorphous alloys containing Fe atoms.

I. Introduction

A lot of experimental studies have been reported on the Fe-rich amorphous alloys containing Zr because these amorphous alloys show some interesting phenomena on the magnetic properties. That is, these alloys reveal a difference in magnetization between zero-field-cooled and field-cooled samples,[1] and the Mössbauer spectroscopy at low temperature indecates that the probability distribution of the magnetic

---

* The 1795th report of the Research Institute for Iron, Steel and Other Metals.

hyperfine fields of Fe atoms spreads over a wide range and shows a low field hump as well as a large peak.[2,3] From the magnetization measurement around the Curie temperature, it is reported that the critical exponents deviate largely from those of three-dimensional Heisenberg ferromagnets.[4]

The Curie temperature of these amorphous alloys has been determined by a few distinct methods. The concentration dependence of the Curie temperature indicates a maximum around 85 at% Fe,[1,5] and this result is qualitatively independent of the determination method. However, the value of the Curie temperature depends on the experimental method; the value of the Curie temperature determined by the Mössbauer thermal scan method[2,3] is smaller than that determined by the magnetization measurements.[1,4,6] This fact shows the Curie temperature of these amorphous alloys must be determined carefully.

In the present study, amorphous Fe-Zr-B alloys are investigated by the Mössbauer spectroscopy and the magnetization measurement. It is found that the difference between the Curie temperatures determined by the Mössbauer thermal scan method and the magnetization measurement results from magnetic inhomogeneity in amorphous Fe-Zr-B alloys and the Mössbauer thermal scan method is very useful for determination of the Curie temperature.

II. Experimental Procedure and Results

The samples were prepared by rapid quenching from the melt using the single roller type quenching apparatus in an atmosphere of argon. The raw materials Fe, Zr and B used in alloy preparation were of 99.9%, 99.6% and 99% purity, respectively. The resulting amorphous ribbons were about 2mm wide and 15μm thick and the amorphous state was verified by X-ray diffraction.

The Mössbauer experiment was performed by using a conventional constant-acceleration type spectrometer (^{57}Co in Rh source). Absorbers with an area of 15 × 15 mm^2 were composed of several cut ribbons placed side by side. At temperatures increasing at a rate of 0.5 K/min , the transmission intensity of the γ-ray was measured at zero velocity.

The magnetization as a function of temperature or of magnetic field was measured using a vibrating-sample magnetometer under magnetic fields up to 18 kOe. A typical heating rate of about 0.5 K/min was maintained during the measurement and the magnetic field was ap-

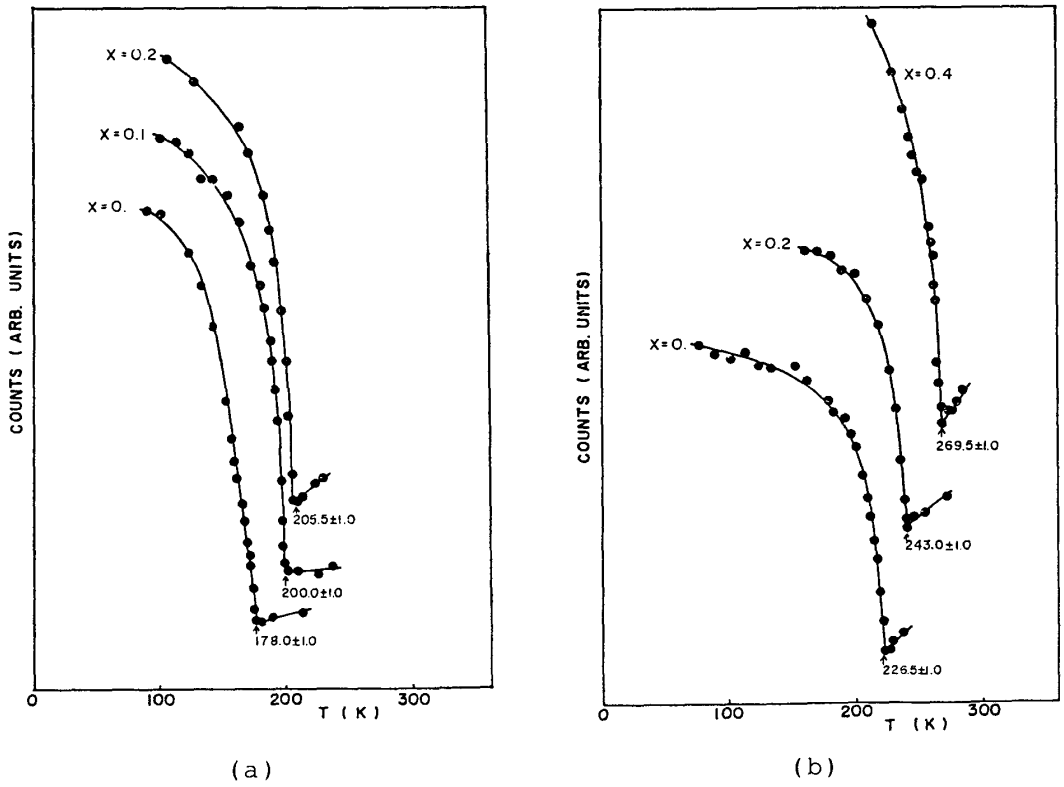

Fig. 1. The transmission rate of the γ-ray at zero velocity as a function of temperature.
(a) $Fe_{92}(Zr_{1-x}B_x)_8$ (b) $Fe_{90}(Zr_{1-x}B_x)_{10}$

plied parallel to the plane of the ribbons.

The Curie temperature (T_C) was determined by measuring the transmission rate of the γ-ray at zero velocity as a function of temperature, and is shown in Fig. 1.[3] Figure 2 shows the temperature dependence of the magnetization of amorphous $Fe_{90}(Zr_{1-x}B_x)_{10}$ (x=0, 0.4) alloys under a magnetic field of 9.5 kOe. It is difficult to determine the value of T_C by the temperature dependence of the magnetization because the magnetization changes sluggishly near T_C. By the conventional method based on the molecular-field theory,[7] the magnetization data were tentatively plotted as isotherms of M^2 *v.s.* H/M (Arrott plots) where H is corrected for demagnetization. These data do not yield a set of straight lines. The Curie temperature for metal=metalloids alloys has been determined with the isotherm that goes though the origin by parabolic extrapolation.[8] In the present case, however, these isothermal data can not be approximated by a parabolic curve. Therefore, as shown in Fig. 3, the present data were rearranged with the plots, M^2 *v.s.* $(H/M)^{1/2}$, to minimize errors result-

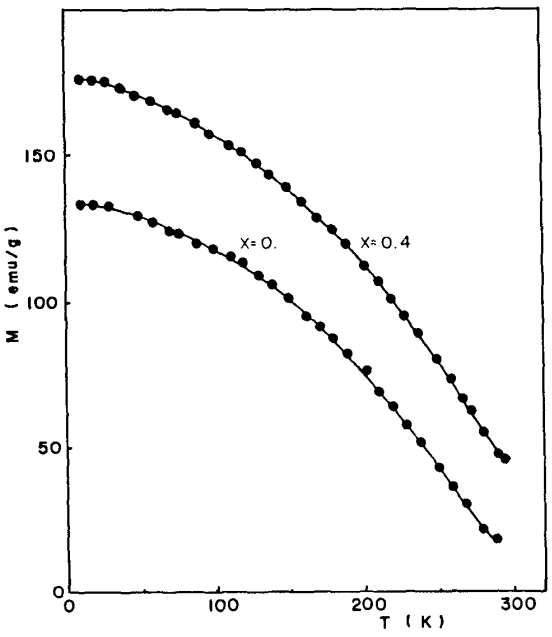

Fig. 2. The temperature dependence of magnetization at 95 kOe for $Fe_{90}(Zr_{1-x}B_x)_{10}$.

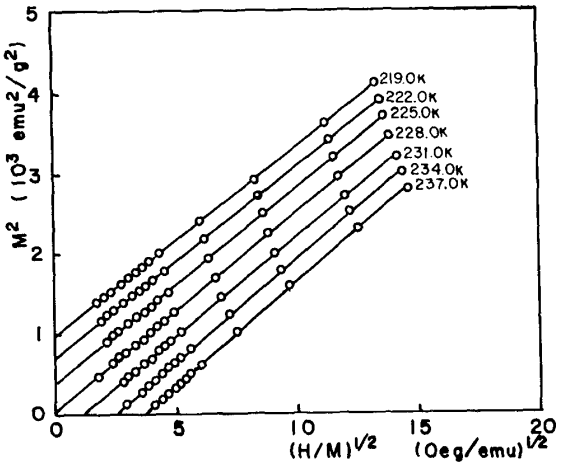

Fig. 3. M^2 *v.s.* $(H/M)^{1/2}$ plots of $Fe_{90}Zr_{10}$ for verious temperature in the vicinity of the Curie temperature. Solid lines were computed using a least squares program.

ing from the asymptotic method, though these deviate slightly from the straight lines (the modified Arrott-plots method). The value of T_c was obtained by the modified Arrott-plots method, where the inverse initial susceptibility is zero.

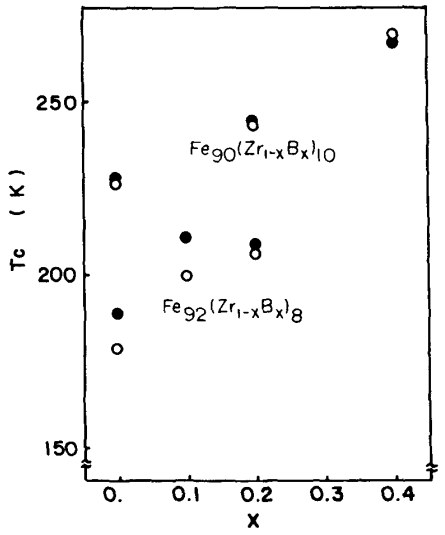

Fig. 4. The concentration dependence of the Curie temperature (T_c). The difference between the results from the Mössbauer thermal scan (open circles)[3] and the modified Arrott-plots methods (closed circles).

Figure 4 shows the concentration dependence of T_c determined by the Mössbauer thermal scan and the modified Arrott-plots methods. For amorphous $Fe_{90}(Zr_{1-x}B_x)_{10}$ alloys, the value of T_c determined by the Mössbauer thermal scan method is in good agreement with that obtained by the modified Arrott-plots method, while for amorphous $Fe_{92}(Zr_{1-x}B_x)_8$ alloys (especially x=0, 0.1), the two methods make a difference over 10K between the values of T_c.

III. Discussion and Conclusion

Since these results suggest that the determination of T_c for amorphous $Fe_{92}(Zr_{1-x}B_x)_8$ alloys is rather troublesome, the data of the transmission rate of the γ-ray at zero velocity were rearranged with the plots, $\Delta N(T)/\Delta N(0.5T_c)$ *v.s.* T/T_c, where $\Delta N(T)=N(T)-N(T_c)$, and N(T) is the count of γ-ray at any temperature. As shown in Fig. 5, the modes of the reduced-temperature dependence of $\Delta N(T)/\Delta N(0.5T_c)$ may be divided into three groups: that is, (1) amorphous $Fe_{92}Zr_8$ alloy whose value of $\Delta N(T)/\Delta N(0.5T_c)$ decreases most rapidly with temperature, (2) amorphous $Fe_{92}(Zr_{0.9}B_{0.1})_8$ and $Fe_{92}(Zr_{0.8}B_{0.2})_8$ alloys whose decreasing rate of $\Delta N(T)/\Delta N(0.5T_c)$ with temperature is intermediate, (3) amorphous $Fe_{90}(Zr_{1-x}B_x)_{10}$ alloys whose value of $\Delta N(T)/\Delta N(0.5T_c)$ decreases most slowly with temperature in the present samples.

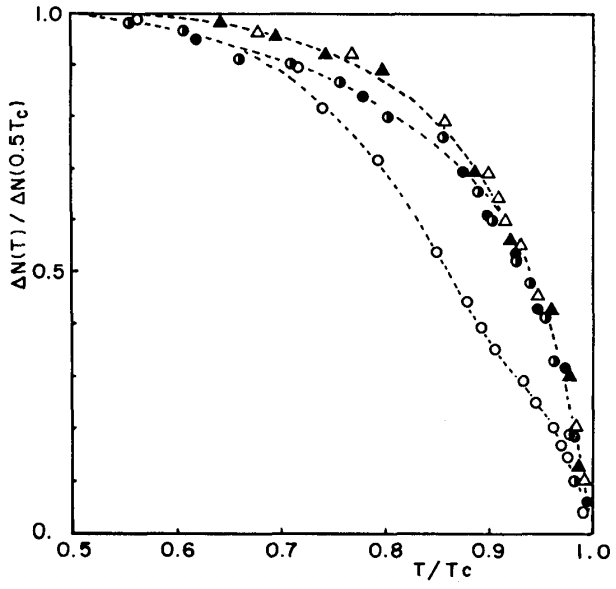

Fig. 5. $\Delta N(T)/\Delta N(0.5T_c)$ *v.s.* T/T_c plots, where $\Delta N(T)=N(T)-N(T_c)$, and N(T) is the count of the γ-ray at any temperature. Open circles; $Fe_{92}Zr_8$; half closed circles: $Fe_{92}(Zr_{0.9}B_{0.1})_8$; closed circles: $Fe_{92}(Zr_{1-x}B_x)_8$; open triangles: $Fe_{90}Zr_{10}$; closed triangles: $Fe_{90}(Zr_{0.6}B_{0.4})_{10}$.

This compositional dependence of the decreasing rate of $\Delta N(T)/\Delta N(0.5T_C)$ with increasing temperature is similar to that of the reduced hyperfine field.[3] Therefore, the temperature dependence of $\Delta N(T)/\Delta N(0.5T_C)$ reflects the magnetic inhomogeneity of amorphous Fe-Zr-B alloys. This inhomogeneity is responsible for the difficulty of determination of T_C.

Figure 6 shows the magnetization of amorphous $Fe_{90}Zr_{10}$ alloy as a function of the magnetic field above T_C. As shown in the previous papers,[2-4] these magnetization curves suggest that the superparamagnetic clusters persist well above T_C. The mean magnetic moment per a cluster ($\bar{M}_C$) can be evaluated by the application of the Langevin function for the observed values, where the distribution of cluster sizes is approximated to be the Gaussian distribution:

$$M = M_S \int_0^\infty P(\mu) L(\alpha) d\mu$$

and M_S is the saturation magnetization, $P(\mu)$ the distribution of cluster sizes, $L(\alpha)$ the Langevin function, $\alpha=\mu H/kT$ and μ the magnetic moment per cluster. The solid lines were computed by using a least squares program. The same analysis as made for amorphous $Fe_{92}Zr_{10}$ alloy was also performed to amorphous $Fe_{90}(Zr_{1-x}B_x)_{10}$ (x=0.2, 0.4) alloys. The values of $\bar{M}_C$ obtained by the above analysis were ploted as a function of temperature in Fig. 7. Since at the temperature

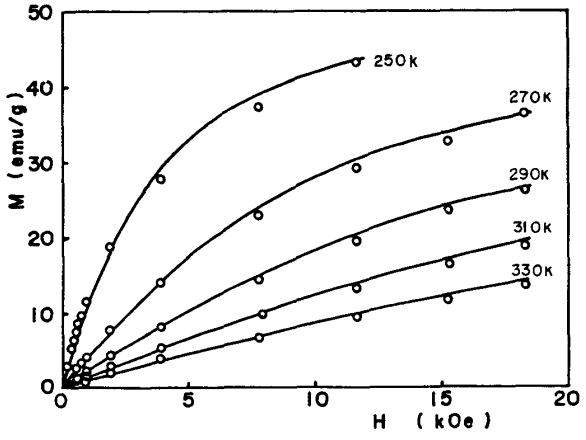

Fig. 6. The magnetic field dependence of the magnetization at several temperatures for $Fe_{90}Zr_{10}$. Solid lines were computed by using a least squares program.

immediately above T_C the value of $\bar{M}_C$ hardly depends on the concentration, T_C appears to be defined by a critical size where the clusters are large enough to correlated with each other. It is not valid that the inverse initial susceptibility and the intrinsic magnetic-ordering temperature are obtained by the modified Arrott-plots method. Hence, the measurement of T_C necessitating external fields is accompanied by a serious problem in the case of the magnetically inhomogenious materials.

The temperature dependence of transmission rate of the γ-ray is influenced by the isomer shifts of source and absorber, the magnetic hyperfine field and the second-order Doppler effect. The isomer shifts of source (Fe in Rh) and amorphous Fe-Zr-B alloys with respect to α-Fe are -0.114 mm/s at room temperature and about 0.05∿0.03 mm/s

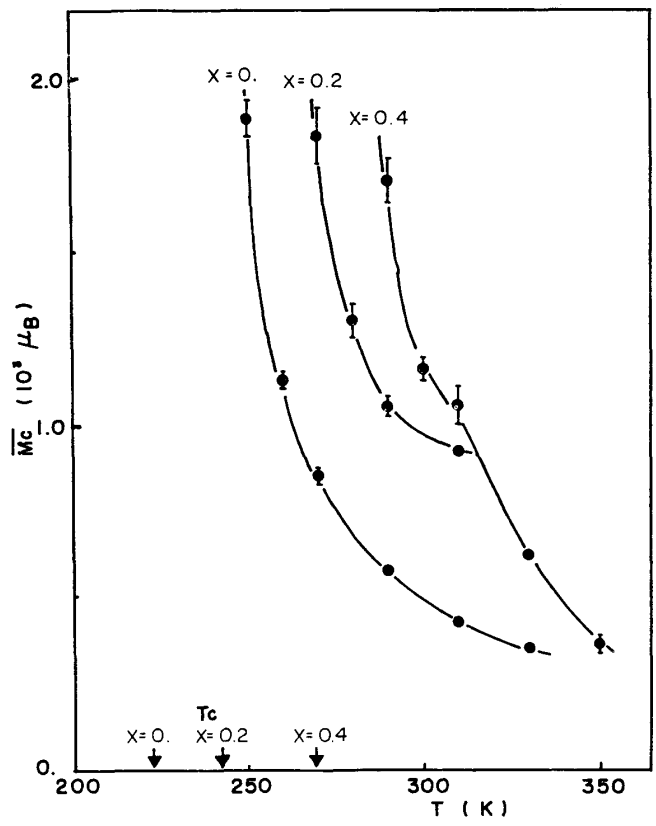

Fig. 7. The concentration and temperature dependence of the mean magnetic moments per cluster ($\bar{M}_C$) for $Fe_{90}(Zr_{1-x}B_x)_{10}$.

at 77K, respectively. The difference of the isomer shifts of source and absorber is negligibly small compared to the line width (about 0.4 mm/s). By the Debye approximation, the temperature dependence of the second-order Doppler shift is given by[9]

$$\delta_{SOD} = -\frac{9}{16}\frac{E_0 k}{mc^2}\left[\theta_D + 8T\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx\right]$$

where E_0 is the energy of the γ-ray and θ_D the Debye temperature of the solid. We evaluated the temperature dependence of the second-order Doppler shift by this equation where the Debye temperature is 280K for amorphous Fe-Zr-B alloys.[10] This value is estimated to be about -0.005 mm/s.deg. in the temperature range of about 150K to 300K. The profile of a Mössbauer spectrum changes much more efficiently through the temperature dependence of the magnetic hyperfine field[3] than through the second-order Doppler shift. For these reasons, the transmission rate of the γ-ray at zero velocity as a function of temperature reflects the temperature dependence of the magnetic hyperfine field in amorphous Fe-Zr-B alloys.

The necessary condition for an obsevable Zeeman splitting of the Mössbauer spectrum is

$$\omega_L \cdot \tau_S \gtrsim 1$$

where ω_L is the nuclear Larmor frequency and τ_S the correlation time of the electron spin. For amorphous Fe-Zr-B alloys, the correlation time of the electron spin can be replaced with that of the magnetic cluster. When the correlation time of the magnetic cluster is sufficiently large, the Zeeman splitting of the Mössbauer spectrum will be observed. In the present samples, however, the clusters just above T_C is too small (about 25 Å) to have a relaxation time long enough to give the Zeeman splitting. Therefore, the Mössbauer thermal scan method is possible to determine the magnetic-ordering temperature below which the clusters are large enough to correlate with each other.

In conclusion, the magnetic inhomogeneity often causes the difficulty in the determination of T_C. The Mössbauer thermal scan method is more reliable than the modified Arrott-plots methods for determining T_C of the magnetically inhomogeneous amorphous alloys containing Fe atoms.

Acknowledgment

We would like to thank Professor T. Masumoto and Mr. H. Kimura for the kind support in the preparation for the amorphous Fe-Zr-B samples.

References

(1) H. Hiroyoshi and K. Fukamichi, J. Appl. Phys., 53 (1982), 2226.
(2) H. Yamamoto, H. Onodera, K. Hosoyama, T. Masumoto and H. Yamauchi, J. Mag. Mag. Mat., 31-34 (1983), 1579.
(3) H. Kobayashi, H. Onodera and H. Yamamoto, J. Phys. Soc. Jpn., to be published.
(4) H. Yamauchi, H. Onodera and H. Yamamoto, J. Phys. Soc. Jpn., 53 (1984), 747.
(5) K.M. Unruh and C.L. Chien, Phys. Rev., B30 (1984), 4968.
(6) S.N. Kaul, Phys. Rev., B27 (1983), 6923.
(7) A. Arrott, Phys. Rev., 108 (1957), 1394.
(8) S.N. Kaul, TEEE Trans. Magn. 20 (1984), 1290, and references therein.
(9) Y. Hazony, Phys. Rev. B7 (1973), 3309.
(10) T. Mizoguchi, M. Akimitsu and S. Takayama, J. Phys. C8 (1980), 698.