Spin-Glass Behavior in Amorphous Ti-Fe Alloys Prepared by High-Rate Sputtering

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Ti_xFe_{100-x} alloy system has been considered to be ferromagnetic. However, it has been confirmed by measurements of the AC magnetic susceptibility and the magnetic cooling effect that the amorphous Ti₅₀Fe₅₀ alloy exhibits the paramagnetic-spin glass transition. The magnetic phase diagram of this system is similar to that of amorphous Zr-Fe alloy system. It is suggested that the triple point consisted of the paramagnetic state, the ferromagnetic state and the spin-glass state is expected to exist in the range from 40 to 45 at.%Ti. The magnetization curves show a relatively easy saturation. The Curie temperature and the magnetic moment per Fe atom decrease with increasing Ti concentration, being similar to the results reported previously.

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I. Introduction

Systematic studies of magnetic properties of amorphous Fe-based alloys have been carried out extensively⁽¹⁾⁽²⁾. According to these results, the magnetic phase diagrams of the amorphous Fe-based alloys are classified into three groups. The first group shows the transition from a paramagnetic to a spin-glass state with decreasing temperature, and the amorphous Y-Fe alloys prepared by sputtering exhibit this transition⁽¹⁾⁽⁴⁾. The second group shows re-entrant spin-glass behavior, which means a paramagnetic state reenters a spin-glass state by way of a ferromagnetic state with decreasing temperature. The amorphous M-Fe alloys (M=La, Ce and Lu) belong to this group⁽¹⁾⁽²⁾. The last group has a wide concentration range of a paramagnetic-ferromagnetic transition, but the re-entrant spin-glass state occurs in a limited concentration range. The amorphous Zr-Fe alloys are classified into this type⁽⁵⁾⁽⁸⁾.

Compared with other amorphous Fe-based alloys, as mentioned above, the amorphous Zr_xFe_{100-x} alloy system is unique because it shows the re-entrant spin-glass behavior in the limited Zr concentration range of about 7.5 < X < 10 and exhibits a paramagnetic-ferromagnetic transition in a wide concentration range of about 10 < X < 45. Besides, it has been confirmed by the measurements of the AC magnetic susceptibility and the magnetic cooling effect that the spin-glass state again appears around X=50⁽⁹⁾.

Both the Curie temperature and the magnetic moment of the amorphous Ti-Fe and Zr-Fe alloys decrease with

decreasing Fe concentration⁽¹⁾⁽⁷⁾⁽⁹⁾⁻⁽¹⁴⁾. It has been reported that the amorphous Ti-Fe alloys are weakly itinerant electron ferromagnets and no spin-glass behavior has been observed in the thermomagnetic curve measured in 15.9 kA·m⁻¹ for an amorphous Ti₅₀Fe₅₀ sputtered alloy⁽¹³⁾⁽¹⁴⁾. However, spin-glass behavior should be measured in lower magnetic fields because it is very sensitive to the applied magnetic fields.

In the present paper, therefore, spin-glass behavior in the amorphous Ti-Fe alloys has been investigated by means of the AC magnetic susceptibility and the magnetic cooling effect. Furthermore, the magnetic properties of the present amorphous alloys have been compared with those of amorphous Zr-Fe alloys.

II. Experimental

Amorphous Ti_xFe_{100-x} alloy samples (X=25, 40, 45 and 50) were prepared by high-rate DC sputtering on a water-cooled Cu substrate. The thickness of samples became about 200 μm by continuous sputtering for 3 days. The Ar gas pressure and the target voltage during sputtering were 5.3 Pa and 1.0 kV, respectively. After sputtering, the Cu substrate was dissolved in a solvent, CrO₃ (0.500 kg)+H₂SO₄ (27 × 10⁻⁶ m³)+H₂O (1.00 × 10⁻³ m³), heated at about 320 K. The amorphous state of the samples was confirmed by X-ray diffraction. The magnetic cooling effect was measured with a SQUID magnetometer. The measurement of the AC magnetic susceptibility was carried out by a mutual induction method in 79.6 A·m⁻¹ and 80 Hz from about 2 to 300 K. The magnetization curves up to 4.38 MA·m⁻¹ were obtained with a SQUID magnetometer.

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III. Results and Discussion

The AC magnetic susceptibility χ_{AC} has been measured in a low magnetic field because the spin freezing temperature T_f is very sensitive to the magnetic field. Figure 1 shows the temperature dependence of χ_{AC} for the amorphous $\text{Ti}_x\text{Fe}_{100-x}$ alloys ($x=25, 40, 45$ and 50) measured in $79.6 \text{ A} \cdot \text{m}^{-1}$ with 80 Hz . As shown in the figure, χ_{AC} for the amorphous $\text{Ti}_{50}\text{Fe}_{50}$ alloy exhibits a cusp around 7.6 K , but no decrease is observed down to 2 K for the amorphous $\text{Ti}_{25}\text{Fe}_{75}$ alloy. Since the temperature dependence for the amorphous $\text{Ti}_{50}\text{Fe}_{50}$ alloy strongly suggests the existence of the spin-glass state, the magnetic cooling effect has been examined.

Figure 2 shows the temperature dependence of the zero-field cooled (ZFC) and the field cooled (FC) magnetization curves measured in $2.39 \text{ kA} \cdot \text{m}^{-1}$ for the amorphous $\text{Ti}_x\text{Fe}_{100-x}$ alloys ($x=25, 40, 45$ and 50). The solid and dotted lines represent the results for ZFC and FC, respectively. The inset shows the curves in order to make hysteresis clear at low temperatures. As shown in the figure, the amorphous $\text{Ti}_{25}\text{Fe}_{75}$ alloy exhibits no hysteresis, showing a ferromagnetic state. The amorphous $\text{Ti}_{40}\text{Fe}_{60}$ alloy exhibits hysteresis below about 4 K , and does a slight decrease in χ_{AC} at the same temperatures as seen from Fig. 1. On the other hand, a drastic increase in the magnetization occurs around 90 K . Therefore, this amorphous alloy is regarded as a re-entrant spin-glass. Both amorphous $\text{Ti}_{50}\text{Fe}_{50}$ and $\text{Ti}_{45}\text{Fe}_{55}$ alloys have a clear hysteresis between the ZFC and FC magnetizations below about 4 K and about 30 K , respectively, where χ_{AC} makes a cusp as seen from Fig. 1. As the spin-glass state

is very sensitive to the magnetic field and the spin freezing temperature T_f decreases with increasing the field⁽¹⁵⁾, the magnetic cooling effect has been examined in the different magnetic fields. Figure 3(a) shows the temperature dependence of the magnetization M for the amorphous

Fig. 2 Temperature dependence of the zero-field cooled (ZFC) and the field-cooled (FC) magnetization curves measured in $2.39 \text{ kA} \cdot \text{m}^{-1}$ for the amorphous $\text{Ti}_x\text{Fe}_{100-x}$ alloys ($x=25, 40, 45$ and 50). The solid and the dotted lines represent the results for ZFC and FC, respectively. The inset exhibits the curves at low temperatures.

Fig. 1 Temperature dependence of the AC magnetic susceptibility for the amorphous $\text{Ti}_x\text{Fe}_{100-x}$ alloys ($x=25, 40, 45$ and 50) measured in $79.6 \text{ A} \cdot \text{m}^{-1}$ and 80 Hz .

Fig. 3 (a) Temperature dependence of the magnetization M for the amorphous $\text{Ti}_{50}\text{Fe}_{50}$ alloy in the field of 2.39 and $7.96 \text{ kA} \cdot \text{m}^{-1}$. (b) The temperature dependence of AC magnetic susceptibility χ_{AC} for the same alloy in $79.6 \text{ A} \cdot \text{m}^{-1}$.

$\text{Ti}_{50}\text{Fe}_{50}$ alloy in the field of 2.39 and $7.96 \text{ kA} \cdot \text{m}^{-1}$, and (b) does the temperature dependence of χ_{AC} measured in $79.6 \text{ A} \cdot \text{m}^{-1}$. The curve measured in $2.39 \text{ kA} \cdot \text{m}^{-1}$ shows a cusp at 4.5 K as given by the arrow, but it is different from the cusp at 7.6 K indicated by the arrow for the χ_{AC} curve in $79.6 \text{ A} \cdot \text{m}^{-1}$. However, no cusp is observed in the curve measured in $7.96 \text{ kA} \cdot \text{m}^{-1}$; that is, spin-glass behavior is completely suppressed above this field. Such behavior is characteristic in many amorphous Fe-based alloys⁽⁹⁾⁽¹⁶⁾. It has been reported that the thermomagnetic curve exhibits no spin-glass like cusp for the sputtered amorphous $\text{Ti}_{50}\text{Fe}_{50}$ alloy in the magnetic field of $15.9 \text{ kA} \cdot \text{m}^{-1}$ ⁽¹³⁾⁽¹⁴⁾, but this magnetic field is too high to confirm spin-glass behavior as mentioned above. From the results of Figs. 1, 2 and 3, it is concluded that the amorphous $\text{Ti}_{50}\text{Fe}_{50}$ and $\text{Ti}_{45}\text{Fe}_{55}$ alloys are spin-glasses, $\text{Ti}_{40}\text{Fe}_{60}$ is a re-entrant spin-glass and that the amorphous $\text{Ti}_{25}\text{Fe}_{75}$ alloy is a ferromagnet.

Figure 4 shows the magnetic phase diagram for the amorphous $\text{Ti}_X\text{Fe}_{100-X}$ alloys. In the present paper, the Curie temperature T_C has been determined as the minimum of dM/dT from Fig. 2, and T_f has been given as the temperature where χ_{AC} exhibits the cusp or the minimum $d\chi_{\text{AC}}/dT$ in Fig. 1. The closed and open circles denote the present results and those obtained by Sumiyama *et al.*⁽¹³⁾⁽¹⁴⁾, respectively. The triangles show the results for the amorphous $\text{Zr}_X\text{Fe}_{100-X}$ alloy⁽¹⁾⁽⁹⁾, for comparison. The solid and the broken lines stand for the Curie temperature T_C and the spin freezing temperature T_f , respectively. As shown in the figure, T_C decreases with increasing Ti concentration. This trend is consistent with the results obtained by other researchers^{(10)(12)–(14)}. It should be noted that the magnetic phase diagram of the amorphous $\text{Ti}_X\text{Fe}_{100-X}$ alloy system is similar to that of the amorphous Zr-Fe alloy system. The triple point consisting of the paramagnetic, the ferromagnetic and the

spin-glass state is observed around $X=47$ for the amorphous Zr-Fe alloy system⁽¹⁾⁽⁹⁾. Therefore, the magnetic behavior in the range from 40 to 45 at.%Ti for the amorphous $\text{Ti}_X\text{Fe}_{100-X}$ alloy system would be interesting in connection with the existence of the triple point. The low-temperature specific heats of the amorphous $\text{Zr}_X\text{Fe}_{100-X}$ alloys ($20 \leq X \leq 80$) have been investigated in the temperature range between 1.5 and 6 K⁽¹⁷⁾. According to these results, the electronic specific heat coefficient γ exhibits a maximum at around $X=55$. Such a large γ is closely correlated to the spin-glass state. Therefore, it is expected that γ also makes a maximum in the range from 40 to 45 at.%Ti for the amorphous Ti-Fe alloy system.

Figure 5 shows the magnetization curves measured at 4.2 K for the amorphous $\text{Ti}_X\text{Fe}_{100-X}$ alloys ($X=25, 40, 45$ and 50). As shown in the figure, these curves exhibit a relatively easy saturation. The magnetic moment μ_{Fe} per Fe atom has been obtained from the saturation magnetization M_S , which is obtained by the law of approach to saturation given by the following expression:

$$M = M_S \left(1 - \frac{a}{H} - \frac{b}{H^2} \right) + \chi_{\text{hf}} H \quad (1)$$

where M is the magnetization, a and b the constants, χ_{hf} the high-field susceptibility and H the magnetic field. In the present paper, the term of b/H^2 in eq. (1) has been ignored because this term is related to magnetocrystalline anisotropy. Shown in Fig. 6 is the concentration dependence of μ_{Fe} for the amorphous $\text{Ti}_X\text{Fe}_{100-X}$ alloys. The closed and open circles denote the results for the present results and the data obtained by Sumiyama *et al.*⁽¹³⁾⁽¹⁴⁾, respectively. The triangles stand for the results of the amorphous $\text{Zr}_X\text{Fe}_{100-X}$ alloys⁽⁷⁾⁽⁹⁾. The value of μ_{Fe} decreases with decreasing Fe concentration, showing a similar tendency to the reported results⁽¹⁰⁾⁽¹³⁾⁽¹⁴⁾. Malozemoff *et al.*⁽¹⁸⁾ have reported the magnetic moments μ_{cal} obtained by the spin-polarized band calculations for a hypothetical $\text{Ti}_{25}\text{Fe}_{75}$ alloy with a AuCu_3 structure in the case of both at the equilibrium and an expanded lattice constants a .

Fig. 4 The magnetic phase diagram for the amorphous $\text{Ti}_X\text{Fe}_{100-X}$ alloys. The closed and open circles denote the present results and the data obtained by Sumiyama *et al.*⁽¹³⁾⁽¹⁴⁾, respectively. The triangles denote the results for amorphous $\text{Zr}_X\text{Fe}_{100-X}$ alloy⁽¹⁾⁽⁹⁾, for comparison. The solid and broken lines stand for the Curie temperature T_C and the spin freezing temperature T_f , respectively.

Fig. 5 The magnetization curves measured at 4.2 K for the amorphous $\text{Ti}_X\text{Fe}_{100-X}$ alloys ($X=25, 40, 45$ and 50).

Fig. 6 The concentration dependence of the magnetic moment μ_{Fe} per Fe atom for the amorphous $\text{Ti}_X\text{Fe}_{100-X}$ alloys ($X=25, 40, 45$ and 50). The closed and open circles denote the present results and the data obtained by Sumiyama *et al.*⁽¹³⁾⁽¹⁴⁾, respectively. The triangles stand for the results of amorphous $\text{Zr}_X\text{Fe}_{100-X}$ alloys⁽⁷⁾⁽⁹⁾.

Table 1 Calculated magnetic moments μ_{cal} for $\text{Ti}_{25}\text{Fe}_{75}$ at the equilibrium and an expanded lattice constants, a ⁽¹⁸⁾. The former and the latter correspond to the experimental moments μ_{obs} for the present amorphous $\text{Ti}_{25}\text{Fe}_{75}$ alloy and the reported amorphous $\text{Zr}_{25}\text{Fe}_{75}$ alloy⁽⁷⁾⁽⁹⁾, respectively.

Calculated	$a/\text{Bohr radius}$	$\mu_{\text{cal}}/\mu_{\text{B}}$	Experimental	$\mu_{\text{obs}}/\mu_{\text{B}}$
$\text{Ti}_{25}\text{Fe}_{75}$ (equilibrium)	6.82	1.31	$\text{Ti}_{25}\text{Fe}_{75}$	0.98
$\text{Ti}_{25}\text{Fe}_{75}$ (expanded)	6.94	1.99	$\text{Zr}_{25}\text{Fe}_{75}$	1.1 ⁽⁷⁾⁽⁹⁾

They have revealed that the slight expansion of the lattice constant remarkably enhances ferromagnetism, as shown in Table 1. Matsuura *et al.* have reported⁽¹⁹⁾ that the interatomic distance of the nearest neighbor Fe-Fe pairs decreases with decreasing the atomic radius of RE in REFe_2 alloys (RE=La, Ce, Pr, Sm, Gd, Dy, Ho and Er). Since the atomic radius of Zr is larger than that of Ti, it may be regarded that observed magnetic moments μ_{obs} for the amorphous $\text{Ti}_{25}\text{Fe}_{75}$ and $\text{Zr}_{25}\text{Fe}_{75}$ ⁽⁷⁾⁽⁹⁾ alloys correspond to the calculated μ_{cal} at the equilibrium and an expanded lattice constants, respectively. Both observed moments qualitatively correspond to the calculated ones shown in the right hand side in the table. That is, the value for the amorphous $\text{Ti}_{25}\text{Fe}_{75}$ alloy is smaller than that for the amorphous $\text{Zr}_{25}\text{Fe}_{75}$ alloy.

IV. Conclusion

The AC and DC magnetic measurements have been carried out for the amorphous $\text{Ti}_X\text{Fe}_{100-X}$ alloys prepared by high-rate DC sputtering in order to investigate spin-glass

behavior. The main results are summarized as follows:

(1) Spin-glass behavior has been confirmed in the amorphous $\text{Ti}_{40}\text{Fe}_{60}$, $\text{Ti}_{45}\text{Fe}_{55}$ and $\text{Ti}_{50}\text{Fe}_{50}$ alloys from the measurements of the AC magnetic susceptibility and the magnetic cooling effect.

(2) The triple point consisting of the paramagnetic, the ferromagnetic and spin-glass state would exist in the range from 40 to 45 at. % Ti.

(3) The magnetic moment per Fe atom of the present alloy system is smaller than that of the amorphous Zr-Fe alloy system and decreases with decreasing Fe concentration.

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