Mössbauer Effect of Metastable *bcc* and Amorphous Phases in $\text{Fe}_{1-x}\text{Ti}_x$ Sputtered Alloys

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Mössbauer spectra were obtained at 290 K and 4.2 K for the metastable *bcc* and amorphous phases of the $\text{Fe}_{1-x}\text{Ti}_x$ sputtered alloys. For $x \leq 0.18$ (the metastable *bcc* phase region), the ferromagnetic sextet was observed at 290 K. A wide hyperfine field distribution and a small hyperfine field component, which appears with an increase in x , imply that the magnetic moment of Fe atoms is dependent on the near neighbor atomic configuration of nonmagnetic Ti atoms. For $x \geq 0.22$ (the amorphous phase region), a considerably broadened sextet was observed at 4.2 K. The average value of the hyperfine field for the amorphous alloy with $x=0.32$ is comparable to that for the Laves phase, TiFe_2 . At 290 K, where the amorphous phase is paramagnetic, a quadrupole splitting was detected and its average magnitude is also comparable to that of the Laves phase.

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I. Introduction

X-ray diffraction and magnetization of sputtered $\text{Fe}_{1-x}\text{Ti}_x$ alloys were reported in the preceding articles⁽¹⁾⁽²⁾. By the sputtering, the single *bcc* phase is extended up to $x=0.18$, the lattice constant of the *bcc* phase is about 0.5% larger than the values extrapolated from the results of bulk Fe-Ti alloys and the amorphous phase is realized for $x > 0.2$. The followings are the characteristic magnetic properties of these alloys. The metastable *bcc* phase is a ferromagnet whose Curie temperature is much higher than room temperature, while the amorphous phase is also a ferromagnet whose Curie temperature is lower than room temperature. The magnetic moments of the amorphous alloys are smaller than those of the metastable *bcc* alloys and the concentration dependence of both magnetic moment and Curie temperature in the amorphous alloys is different from those in the equilibrium Laves phase, TiFe_2 ⁽²⁾⁽³⁾.

Since the magnetic hyperfine field splitting and the electric quadrupole splitting found in the Mössbauer spectra give a microscopic view

of the magnetic and structural properties of Fe alloys, this paper deals with the experimental results of the Mössbauer effect on the sputtered $\text{Fe}_{1-x}\text{Ti}_x$ alloys ($x=0-0.4$) from this view point.

II. Experimental Procedures and Results

Samples were prepared on polyimide film substrates by a conventional rf sputtering method as described in the preceding articles⁽¹⁾⁽²⁾. The Mössbauer effect measurements were carried out at 290 K and 4.2 K by a constant acceleration type spectrometer using a ^{57}Co source doped in Cu.

Figure 1 shows the Mössbauer spectra at 290 K for the sputtered $\text{Fe}_{1-x}\text{Ti}_x$ alloys with $x \leq 0.2$. A ferromagnetic sextet is predominant in the single *bcc* phase region, $x \leq 0.18$. A central peak arises as an amorphous phase, which is paramagnetic at 290 K, appears for $x=0.2$. The linewidth of the sextet increases with the increase in x , which is ascribed to the distribution of hyperfine fields and electric field gradients caused by the random near neighbor configuration of ^{57}Fe atoms. Each spectrum was fitted by a superposition of sets of the six Lorentzians with different Zeemann splittings, leading to the hyperfine field distribution⁽⁴⁾⁽⁵⁾. In the analysis, the halfwidth of a Lorentzian was assumed to be 0.25 mm/s and the isomer shift and the intensity ratio of the second and fifth peaks to the others were adjusted to get

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Fig. 1 Mössbauer spectra at 290 K for $\text{Fe}_{1-x}\text{Ti}_x$ sputtered alloys with $x \leq 0.2$.

the best fitting. The contribution of the electric field gradient was neglected for simplicity. Figure 2 shows the obtained hyperfine field distribution curves at 290 K for $x \leq 0.18$. As x increases, the main peak shifts slightly toward the lower field side, its width becomes wider and a small and broad peak appears below 150 kOe.

The Mössbauer spectra at 290 K for the $\text{Fe}_{1-x}\text{Ti}_x$ alloys with $x > 0.2$, plotted on the expanded velocity-scale in Fig. 3, reveal that the linewidth for $x = 0.22$ is much wider than the natural linewidth of ^{57}Fe and a doublet structure can be seen for $x \geq 0.28$. These phenomena are probably ascribed to a quadrupole splitting in the amorphous alloys⁽⁶⁾⁽⁷⁾, even though the spectra are broadened by a distribution of the electric field gradient. Each spectrum was fitted by a superposition of sets of two Lorentzians with different magnitudes of quadrupole splitting, QS , leading to the distribution of QS ⁽⁸⁾. Here, the halfwidth of a Lorentzian was

Fig. 2 Hyperfine field distribution for *bcc* $\text{Fe}_{1-x}\text{Ti}_x$ sputtered alloys at 290 K. The smooth curves are obtained by Window's method⁽⁴⁾ and the histograms by Hesse's method⁽⁵⁾.

assumed to be 0.25 mm/s and the isomer shift was adjusted to get the best fitting. As shown in Fig. 4, the average value of QS is about 0.3 mm/s, being almost independent of the alloy concentration and comparable to the quadrupole splitting for the Laves phase, TiFe_2 ⁽⁹⁾⁽¹⁰⁾.

At 4.2 K, where the amorphous phase is ferromagnetic, the spectra shown in Fig. 5 are very broad because of a hyperfine field distribution, which are in marked contrast to the clearly split sextet observed for the Laves phase at low temperatures⁽⁹⁾. However, the halfwidth of the absorption spectrum for $x = 0.32$ which almost corresponds to the composition, TiFe_2 , is roughly estimated as 3 mm/s. This value is almost the same as the separation between the first and sixth peaks of the clearly split sextet

Fig. 3 Mössbauer spectra at 290 K for amorphous $\text{Fe}_{1-x}\text{Ti}_x$ sputtered alloys.

observed for the Laves phase⁽⁹⁾⁽¹⁰⁾. The distribution of the hyperfine fields for the amorphous $\text{Fe}_{1-x}\text{Ti}_x$ alloys was obtained by the same analysis applied to the result of the *bcc* $\text{Fe}_{1-x}\text{Ti}_x$ alloys and is shown in Fig. 6. With the increase in x , the broad distribution peak shifts to the lower hyperfine field side.

III. Discussion

In Fig. 2, the small satellite peak is observed in the low hyperfine field region together with the large main peak in the high hyperfine field region. With the increase in x , the fraction of satellite peak, A , increases, while the main peak slightly decreases and shifts toward the lower

Fig. 4 Distributions of quadrupole splitting for amorphous $\text{Fe}_{1-x}\text{Ti}_x$ sputtered alloys at 290 K.

hyperfine field side. This doubly peaked character in hyperfine field distribution is a common feature in the *bcc* Fe alloys with nonmagnetic elements such as Fe-V and Fe-Cr⁽¹¹⁾⁽¹²⁾. Since in these alloys the magnetic moment of Fe atoms is sensitive to the near neighbor atomic configuration, the Fe atoms with a large number of nonmagnetic near neighbor atoms carry small or no magnetic moments, giving rise to the low hyperfine field component in the distribution curve. Since Ti is a strongly perturbing element in the Fe alloys as well⁽¹⁶⁾, the magnetic moment of Fe atoms must be influenced by the nearest Ti atoms. Simply assuming that the magnetic moment of Fe atoms becomes zero as the number of nearest Ti atoms reaches the

Fig. 5 Mössbauer spectra at 4.2 K for amorphous $\text{Fe}_{1-x}\text{Ti}_x$ sputtered alloys.

critical number, n_c , in the random solid solution, the concentration dependence of A is roughly explained by $n_c=3$, as shown in Fig. 7(a). Furthermore, this assumption explains well the concentration dependence of average magnetic moment of Fe atoms as shown in Fig. 7(b)⁽²⁾, where the Ti atom is assumed to carry no magnetic moment.

In the amorphous alloys, the widely distributed quadrupole splitting has been explained on the basis of the dense random packing of hard sphere (DRPHS) model, where the distribution of quadrupole splitting was ascribed to Voronoi polyhedra⁽¹³⁾ or the random angular and radial distribution of atoms at the near neighbor position in the amorphous alloys⁽¹⁴⁾. However, the present amorphous $\text{Fe}_{1-x}\text{Ti}_x$ alloys show the rather clear quadrupole splitting for $x \geq 0.28$, while only show a broad peak for $x < 0.28$. These concentration-dependent features of quadrupole splitting are inconsistent with the DRPHS model which gives a concentration-insensitive quadrupole splitting. On

Fig. 6 Hyperfine field distribution for amorphous $\text{Fe}_{1-x}\text{Ti}_x$ sputtered alloys at 4.2 K obtained by the same methods as in Fig. 2.

the contrary, the similar magnitude of quadrupole splitting between the amorphous phase and the Laves phase and the above mentioned concentration dependent behavior of quadrupole splitting lead to a more simple interpretation that the short range atomic arrangement of the amorphous phase resembles to that of the Laves phase⁽¹⁵⁾. In the ferromagnetic state (at 4.2 K), the distribution of hyperfine field is remarkable, where the average value of hyperfine field for $x=0.32$ is comparable to that of the Laves phase⁽⁹⁾⁽¹⁰⁾. Since the magnetic moment of Fe atoms in the Laves phase is

Fig. 7 (a) Concentration dependence of the volume fraction of low hyperfine field component, A , ($\bullet$) and the probability of finding an Fe atom with more than three Ti nearest neighbors, ($\circ$) for bcc $Fe_{1-x}Ti_x$ sputtered alloys. (b) Concentration dependence of magnetic moment per Fe atom, $\blacktriangle$: experimental results at 290 K and $\triangle$: the estimated ones from Fig. 7(a).

sensitive to the near neighbor atomic configuration⁽⁹⁾, the widely distributed hyperfine field has been expected in the present amorphous alloys.

Concludingly, for the $Fe_{1-x}Ti_x$ sputtered alloys, the Mössbauer effect measurements give the same phase boundary of the metastable phases as estimated from the X-ray diffraction and magnetization measurements. The bcc alloys reveal a wide distribution of hyperfine field and very small hyperfine field components. For the amorphous alloys, the average quadrupole splitting and hyperfine field are almost the

same as those for the Laves phase even though the distribution of these values are remarkable.

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