RAPID PUBLICATION

Microstructure of Carbide-Dispersed Nanocrystalline Fe-Ta-C Films

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Nanocrystalline structure of soft magnetic Fe-Ta-C films crystallized from an amorphous state has been investigated. High-resolution transmission electron microscopy (HRTEM) revealed that tantalum carbide particles much smaller than iron grains are dispersed at the grain boundaries (mostly at tripple junctions) of iron grains. Such a configuration of the carbides hardly interrupts the intergranular magnetic coupling which reduces the effective magnetocrystalline anisotropy. It was also found by both HRTEM and temperature dependence of magnetization and coercivity that there is no distinct residual amorphous phase in the nanocrystalline Fe-Ta-C films, unlike the Fe-Cu-Nb-Si-B alloys. It was proved that the substance stabilizing the nanocrystallites in the Fe-Ta-C films is not an amorphous phase but the tantalum carbide which is thermally more stable.

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I. Introduction

Sputter-deposited amorphous Fe-Ta-C films crystallize into a nanocrystalline state by annealing at temperatures higher than 700 K⁽¹⁾. These nanocrystalline films simultaneously show high saturation magnetization, good soft magnetic properties and high thermal stability, which are suitable for use in magnetic heads. The high stability of the nanocrystalline structure is attributed to the suppression of grain growth by finely dispersed tantalum carbide (TaC: NaCl-type) particles, in contrast to the Fe-Cu-Nb-Si-B alloys⁽²⁾, for which the substance stabilizing the nanocrystallites was reported to be an amorphous phase⁽³⁾⁻⁽⁵⁾. Since the exchange and/or dipole-dipole interactions between iron grains play an important role in averaging out the magnetocrystalline anisotropy⁽⁶⁾⁽⁷⁾, the configuration of such non-magnetic carbides and the structure of grain boundaries are considered to have a great influence on the soft magnetic properties. However, the microstructure of Fe-Ta-C films has not been clarified in detail. The purpose of the present work is to reveal microstructure of the carbide-dispersed films by transmission electron microscopy and magnetic measurements.

II. Experimental Procedure

Fe-Ta-C films with 5 μm in thickness were deposited

by rf sputtering and annealed at various temperatures. Relative permeability μ and coercivity H_c at room temperature were measured using the figure-8 coil method and a dc B - H tracer, respectively. A vibrating sample magnetometer was used for measuring the temperature dependence of saturation magnetization I_s and coercivity. The thin samples for transmission electron microscopy (TEM) were prepared by peeling the films from substrates and ion milling both sides of them. A 400 kV TEM (JEM-4000EX) equipped with a top entry goniometer was used for high-resolution observations and a 200 kV TEM (JEM-2000EX) for normal observations.

III. Results and Discussion

Figure 1 shows the annealing temperature dependence of (a) lattice spacing of iron measured by X-ray diffraction, (b) saturation magnetization I_s , (c) relative permeability $|\mu|$ at 1 MHz, and (d) coercivity H_c , for Fe_{81.4}Ta_{8.3}C_{10.3} film. These were measured at room temperature after annealing for 1.2 ks at each temperature. The amorphous film crystallizes into the mixture of iron and tantalum carbide. After the crystallization around 700 K, the iron crystallites at first are tetragonally deformed, probably owing to the supersaturated dissolution of carbon. This gradually approaches to pure iron as the annealing temperature increases, as seen in Fig. 1(a). Along with that change in iron crystallites, I_s slightly but constantly increases even after crystallization. On the other hand, since the grain growth of nanocrystallites is

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Fig. 1 Annealing temperature dependence of (a) lattice spacing d of iron, (b) saturation magnetization I_s , (c) relative permeability $|\mu|$ at 1 MHz, and (d) coercivity H_c , for the $\text{Fe}_{81.4}\text{Ta}_{8.3}\text{C}_{10.3}$ film.

very sluggish, the high permeability and low coercivity are maintained even after annealing at 973 K.

Figure 2 shows TEM images and an electron diffraction pattern of the film annealed at 973 K for 1.2 ks. As seen in the dark-field image (b) taken from $\{111\}$ reflection of tantalum carbides (TaC: NaCl-type), the grain

size of carbides is from 3 to 7 nm in diameter. Further, the grain size of iron is from 15 to 25 nm, as seen in the bright-field image or the dark-field image (a) taken from $\{110\}$ reflection of iron. The high-resolution electron micrograph of the same sample is shown in Fig. 3. It is easy to distinguish between iron and tantalum carbide grains by their grain size which is already revealed from the dark-field observations, even in the grain whose lattice image is not distinct because of the misorientation of zone axes. Rough fringes seen in the iron grains at the right and left hand in Fig. 3 may be due to a thin oxide layer formed on the surface of iron grains, although the diffraction pattern does not show any distinct reflections other than iron and TaC. As seen in Fig. 3, tantalum carbides are dispersed at the grain boundaries (mostly at triple junctions) of iron grains, not in the iron grains. Nevertheless, adjacent iron grains are in contact through wide area of grain boundaries, as indicated with arrowheads in the image, because the tantalum carbides are much smaller than iron grains. This contact between iron grains enables exchange and dipole-dipole interactions which make the magnetization of each iron grain nearly parallel, and which result in good soft magnetic properties. Since the grain boundary does not look straight, it seems not yet in an equilibrium state and a possibility of the existence of an amorphous phase is still not to be denied. However, it is obvious that a distinct amorphous phase as that observed in the nanocrystalline Fe-Cu-Nb-Si-B alloy⁽⁵⁾ does not exist in the Fe-Ta-C film. That is also supported from the fact that the iron grains in the Fe-Ta-C film do not have a global shape unlike those in the Fe-Cu-Nb-Si-B alloy.

The microstructure should also be revealed for more soft magnetic film annealed at lower temperatures. For that film, however, it was difficult to prepare sufficiently

Fig. 2 TEM images and electron diffraction pattern of the $\text{Fe}_{81.4}\text{Ta}_{8.3}\text{C}_{10.3}$ film annealed at 973 K for 1.2 ks. The dark-field images, (a) and (b) were taken with an objective aperture indicated with the circles in the diffraction pattern.

Fig. 3 High-resolution electron micrograph of the $\text{Fe}_{81.4}\text{Ta}_{8.3}\text{C}_{10.3}$ film annealed at 973 K for 1.2 ks. The grain boundaries between iron grains are indicated with arrowheads.

Fig. 4 High-resolution electron micrograph of the $\text{Fe}_{81.4}\text{Ta}_{8.3}\text{C}_{10.3}$ film annealed at 823 K for 1.2 ks. The grains of tantalum carbide are indicated with arrowheads.

Fig. 5 Temperature dependence of saturation magnetization I_s for the $\text{Fe}_{81.4}\text{Ta}_{8.3}\text{C}_{10.3}$ film, measured by heating the film after annealing at various temperatures.

thin sample less than the grain size because the grain size of the tantalum carbide is from 1 to 3 nm after annealing at 823 K for 1.2 ks. Figure 4 shows the high-resolution electron micrograph of the Fe-Ta-C film annealed at 823 K for 1.2 ks. The grains indicated with arrowheads are discerned as TaC judging from their lattice spacing (0.26 nm) close to that of {111} plane of TaC (NaCl-type). In the image, the microstructure is not so clear as Fig. 3 because grains is too small. However, it seems improbable that the distinct amorphous phase like that in the Fe-Cu-Nb-Si-B alloy exists. That is needed to be verified by the other methods.

If the residual amorphous phase is ferromagnetic and its Curie temperature T_C is much lower than that of the crystalline phase, the curve of temperature dependence of magnetization and/or coercivity shows anomaly around its T_C . It was reported that the residual amorphous phase in the Fe-Cu-Nb-Si-B alloy was successfully detected by those measurements⁽³⁾⁽⁷⁾. In Fig. 5, temperature dependence of I_s for $\text{Fe}_{81.4}\text{Ta}_{8.3}\text{C}_{10.3}$ films is shown. All these curves are heating curves. The T_C of the as-deposited amorphous film (a) is around 360 K. This increases by about 15 K after annealing at temperatures lower than the crystallization temperature, as seen in the curve (b). The curve (c) is for the film annealed at 695 K for 1.2 ks and just crystallized halfway. This curve shows a distinct inflection point which characterizes the coexistence of crystalline and amorphous phases. However, the film annealed at this temperature shows only poor soft magnetic properties as seen in Fig. 1. This implies that the residual amorphous phase is not essential for soft magnetic properties in the Fe-Ta-C films. The curve of the film annealed at 823 K for 1.2 ks (d) shows no inflection point at any temperatures lower than 823 K.

Fig. 6 Temperature dependence of coercivity H_c for the $\text{Fe}_{81.4}\text{Ta}_{8.3}\text{C}_{10.3}$ film, measured by heating the film after annealing at 823 K for 1.2 ks.

The inflection around 823 K is due to the exhaustion of carbon out of the iron grains because it is irreversible. The cooling curve almost follows along the heating curve (e) of the film annealed at 973 K for 1.2 ks. The curve (e) also shows that a ferromagnetic phase in the film is bcc-iron only.

Even if the volume fraction of amorphous phase is very small, very thin layers at grain boundaries can more sensitively be detected by temperature dependence of H_c , because the exchange interaction is considered to be interrupted with only a few non-magnetic layers. If there is an amorphous phase with low- T_C , the H_c rapidly increases at higher temperatures than that T_C , because the magnetization in each iron grain becomes almost isolated. Figure 6 shows the temperature dependence of H_c (heating curve) for the $\text{Fe}_{81.4}\text{Ta}_{8.3}\text{C}_{10.3}$ film after annealing at 823 K for 1.2 ks. Since the low H_c is maintained until its pre-annealing temperature (823 K), the amorphous phase with low T_C does not exist, or even if it remains, it does not cover all the grain surfaces so as to hardly affect the H_c . The increase in H_c at higher temperature than 823 K is an irreversible change due to the grain growth.

Consequently, the residual amorphous phase in nanocrystalline Fe-Ta-C films is not essential for either soft magnetic properties or stabilizing the nanocrystallites unlike the Fe-Cu-Nb-Si-B alloys. The substance stabilizing the nanocrystallites in Fe-Ta-C films is tantalum carbides which are more stable than an amorphous phase; that is one of the reasons for higher thermal stability of soft magnetic properties.

IV. Conclusions

The microstructure of nanocrystalline Fe-Ta-C films crystallized from an amorphous state has been characterized as follows:

(1) It has been directly observed that the tantalum carbide particles much smaller than the iron grains are dispersed at the grain boundaries (mostly at tripple junctions) of iron grains. Such a configuration of carbide particles hardly interrupt the magnetic interaction between iron grains.

(2) A distinct residual amorphous phase as reported for the Fe-Cu-Nb-Si-B alloys was not found in the Fe-Ta-C films annealed at temperatures higher than 823 K. This suggests that the residual amorphous phase is not essential for either soft magnetic properties or its thermal stability in the Fe-Ta-C films.

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