

## THE EFFECT OF NITROGEN ON THE MICROSTRUCTURE AND THE CORROSION RESISTANCE OF Fe-Hf-C-N THIN FILMS

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**Abstract** - We have studied the effect of the nitrogen on the microstructure, thermomagnetic properties and corrosion resistance of Fe-Hf-C-N nanocrystalline thin films with high permeability and high saturation magnetization. These films were fabricated by reactive sputtering in Ar+N<sub>2</sub> plasma using an rf magnetron sputtering apparatus. As P<sub>N<sub>2</sub></sub> increases, the microstructure changes from amorphous to crystalline  $\alpha$ -Fe phase and again returns to amorphous one. Spin wave stiffness constant increases with P<sub>N<sub>2</sub></sub> until 5% P<sub>N<sub>2</sub></sub>, and then decreases with the further increase. This trend corresponds well with that of the microstructure with increasing P<sub>N<sub>2</sub></sub>. The Fe-Hf-C-N films with over 3% P<sub>N<sub>2</sub></sub> show higher corrosion resistance than the N-free Fe-Hf-C films. The Fe-Hf-C-N films are considered to have high potentials for the head core materials suitable for high density recording systems, owing to their excellent soft magnetic properties and corrosion resistance.

### I. INTRODUCTION

There has long been an interest in high-density technology of magnetic recording. Magnetic recording density has been increasing year by year with a corresponding increase in the coercive force of the media. To effectively cope with high coercivity magnetic media, the head core material is required to have high saturation magnetization and high permeability. Thus recent investigations searching for new soft magnetic materials have been directed to Fe-based nanocrystalline films.[1] It is so far reported that the addition of metalloids such as B, C and N in Fe-M (M; transition metals such as Hf, Ta, Zr, etc.) is effective to improve soft magnetic properties and thermal stability.[2-6] In a previous paper, we reported that Fe-Hf-C-N films exhibit excellent soft magnetic properties.[7] In order to understand the correlation between the magnetic properties and the microstructure of these films, it is important to investigate the crystallization behavior of the remaining amorphous phase of as-deposited Fe-Hf-C-N films. The understanding of corrosion behavior is also important, since the incorporation of soft magnetic materials into a device such as magnetic head requires that it be exposed to processing environments which will affect the materials reliability. In this paper, we investigate the effects of nitrogen content on

the microstructure, thermomagnetic properties and corrosion resistance for Fe-Hf-C-N thin films.

### II. EXPERIMENTAL

Fe-Hf-C-N films were fabricated by reactive sputtering in Ar+N<sub>2</sub> plasma using an rf magnetron sputtering apparatus. The target consisted of an Fe disc with small pieces of Hf and C. The partial pressure of nitrogen gas (P<sub>N<sub>2</sub></sub>) was controlled in the range of 0~10% keeping the total gas pressure constant at 1x10<sup>-3</sup> Torr. The films of 1  $\mu$ m thickness and 10 mm diameter were deposited onto Corning 7059 glass substrates. The composition of films was analyzed by AES, and some of films also by RBS. The films were annealed at 350 ~ 700 °C for 30 min in vacuum. The saturation magnetization (4 $\pi$ M<sub>s</sub>) and coercive force (H<sub>c</sub>) were measured by a VSM. Thermomagnetic analysis was performed in the temperature range of liquid helium temperature to 800 °C using a VSM and a SQUID. The effective permeability ( $\mu_{eff}$ ) was measured at 1 MHz by an impedance analyzer using a horse-shoe shaped ferrite core. The microstructure was investigated by a XRD. Corrosion resistance was determined by the change of the coercivity and the saturation magnetization after exposing the films to 80°C and 80% relative humidity.

### III. RESULTS AND DISCUSSION

#### A. Microstructural Variation with N Content

In the Fe-Hf-C-N alloys, it is expected that Hf has the strong tendency to react with C and N forming carbonitride. So we investigate the microstructural change of  $\text{Fe}_{84.6}\text{Hf}_{8.5}\text{C}_{6.9}$  alloys with increasing  $P_{N_2}$ . Fig. 1 shows X-ray diffraction patterns of as-deposited Fe-Hf-C-N films as a function of  $P_{N_2}$ . As  $P_{N_2}$  increases, the microstructure changes from amorphous to crystalline  $\alpha$ -Fe phase and at 10%  $P_{N_2}$  again returns to amorphous one. In the  $P_{N_2}$  region where the crystallinity increases, the origin of phase transition with increasing  $P_{N_2}$  is considered to be due to the fact that N reacts more readily with Hf rather than C does, owing to larger magnitude of free energy of formation of HfN than HfC. As  $P_{N_2}$  increases, the Fe-Hf-C-N amorphous matrix contains less Hf content owing to the precipitation of Hf(C,N) from the matrix. This may lower the crystallization temperature of the remaining amorphous phase and resultantly some parts of the matrix are crystallized. The formation of an amorphous phase at high  $P_{N_2}$  may be due to the accumulated strain induced by the incorporation of large amount of N into  $\alpha$ -Fe lattice.[8,9]

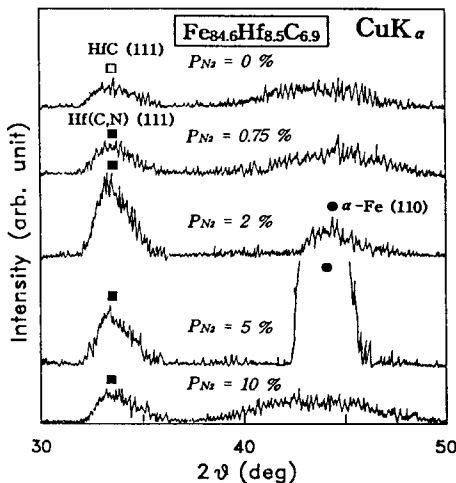


Fig. 1 XRD patterns of as-deposited Fe-Hf-C-N films as a function of nitrogen partial pressure( $P_{N_2}$ ).

#### B. Variation of Thermomagnetic properties with N Content

We performed a thermomagnetic analysis in order to further understand the crystallization behavior of the remaining amorphous phase of as-deposited films. The results are shown in Fig. 2. As  $P_{N_2}$  increases, Curie temperature of amorphous phase ( $T_{c,am}$ ) increases and crystallization temperature ( $T_x$ ) of amorphous phase decreases. And also the shape of change in magnetization near  $T_x$  becomes shallow. This means that the fraction of remaining amorphous phase is decreased and crystallinity is improved. With a further increase in  $P_{N_2}$  exceeding 5%, on the contrary, the shape of change in magnetization near  $T_x$  becomes deep again, indicating that the fraction of amorphous phase is increased again. As for the crystallization behavior, the amorphous precursor of Fe-Hf-C-N is different from that of N-free Fe-Hf-C. The former has high  $T_c$  and low  $T_x$  compared to the latter, and the former is crystallized into  $\alpha$ -Fe through 2 steps.

A number of studies have been reported on the magnetic behavior at low temperatures both crystalline and amorphous ferromagnetic materials. At low temperature, the magnetization  $M_s(T)$  is well described in terms of the spin wave approximation.[10]

$$\frac{M_s(0) - M_s(T)}{M_s(0)} = B T^{3/2} \quad (1)$$

The Bloch coefficient B is related to the spin wave stiffness constant,  $D_m$ , through the expression

$$B = [2.612 \cdot g \mu_B / M_s(0)] (k_B / 4 \pi D_m)^{3/2} \quad (2)$$

where  $g$  is the spectroscopic splitting factor,  $\mu_B$  the Bohr magneton,  $k_B$  the Boltzmann constant, and  $D_m$  spin-wave stiffness constant. The Bloch coefficient B can be determined by fitting the magnetization curve. Fig. 3 shows the  $T^{3/2}$  behavior of the low temperature magnetization in Fe-Hf-C-N films. Rearranging the eq.(2) yields

$$D_m = [2.612 \cdot g \mu_B / M_s(0) B]^{2/3} (k_B / 4 \pi) \quad (3)$$

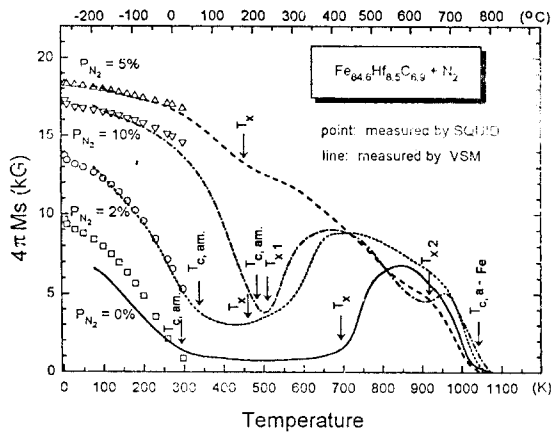


Fig. 2 Thermomagnetic diagram of Fe-Hf-C-N films as a function of nitrogen partial pressure ( $P_{N_2}$ ).

The value of spectroscopic splitting factor  $g$  is assumed to be 2.[11] Using the values  $B$ ,  $M_s(0)$  and  $g$ , the spin wave stiffness constants ( $D_m$ ) are calculated and the results are listed in Table 1. For comparison, the results for pure Fe and an Invar alloy are also given in Table 1. Table 1 shows that N-free Fe-Hf-C amorphous film has smaller spin wave stiffness constant than the Invar alloy. Note that low spin wave stiffness constant means large Invar effect.  $D_m$  increases with  $P_{N_2}$ , having the maximum value at 5%  $P_{N_2}$ , and then decreases with the further increase of  $P_{N_2}$ . This trend corresponds with the change of microstructure with increasing  $P_{N_2}$  shown in Fig. 1. It is interpreted that the saturation magnetization of amorphous alloy decreases mainly by the thermal excitation of magnon due to the fluctuation of exchange coupling. The Fe-Hf-C-N films with 5%  $P_{N_2}$  exhibit the effective permeability of about 2000 and the saturation magnetization of 14 kG, even if in as-deposited state, due to their high  $D_m$ .

### C. Variation of Corrosion Resistance with N Content

Figs. 4 and 5 show the change of the saturation magnetization and the coercive force of Fe-Hf-C-N films, respectively, as a function of time exposed to the corrosive environment described in Sec. II. In the N-free Fe-Hf-C film, the saturation

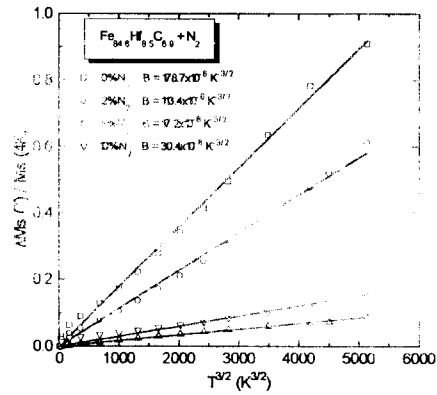


Fig. 3  $T^{3/2}$  temperature dependence of  $\Delta M_s(T)/M_s(4\text{ K})$  for the as-deposited Fe-Hf-C-N films.

Table 1 Saturation magnetization ( $M_s(4\text{ K})$ ), Bloch coefficient ( $B$ ) and spin wave stiffness constant ( $D_m$ ) for the as-deposited Fe-Hf-C-N films.

$P_{N_2}$ (%)	Composition	$M_s$ (emu/cm <sup>3</sup> )	$10^{-6} B$ (K <sup>-3/2</sup> )	$D_m$ (meVÅ <sup>2</sup> )
0	Fe <sub>0.6</sub> Hf <sub>0.5</sub> C <sub>6.9</sub>	766	178.7	34.3
2	Fe <sub>0.4</sub> Hf <sub>0.2</sub> C <sub>6.7</sub> N <sub>3.7</sub>	1091	113.4	36.7
5	Fe <sub>0.1</sub> Hf <sub>0.8</sub> C <sub>5.9</sub> N <sub>9.2</sub>	1458	17.2	106.4
10	Fe <sub>0.2</sub> Hf <sub>0.7</sub> C <sub>5.6</sub> N <sub>16.4</sub>	1373	30.4	75.8
	Fe	---	3.4	285
	Fe <sub>85</sub> Ni <sub>15</sub> (Invar Alloy)	---	---	59

magnetization decreases drastically with increasing the exposure time. On the other hand, Fe-Hf-C-N films with over 3%  $P_{N_2}$  hold almost constant saturation magnetization until long exposure time indicating high corrosion resistance. This trend is similar to that observed in Fe-N films where the corrosion resistance increases with increasing N content.[13]

## IV. CONCLUSIONS

We investigated the effect of nitrogen on the microstructure, thermomagnetic properties and corrosion resistance for Fe-Hf-C-N films. As  $P_{N_2}$  increases, the microstructure changes from amorphous to crystalline  $\alpha$ -Fe phase and again returns to amorphous one at high  $P_{N_2}$ . Spin wave stiffness constant, which shows magnetic behavior

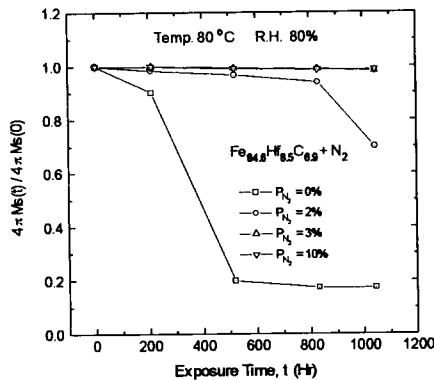


Fig. 4 Change of saturation magnetization for the Fe-Hf-C-N films as a function of exposure time under the corrosive atmosphere.

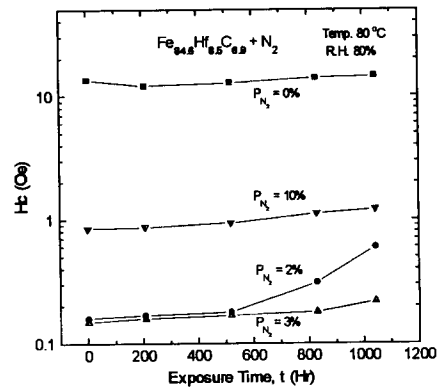


Fig. 5 Change of coercive force for the Fe-Hf-C-N films as a function of exposure time under the corrosive atmosphere.

at low temperatures, increases with  $P_{Nz}$  until 5%  $P_{Nz}$ , and then decreases with the further increase of  $P_{Nz}$ . This trend corresponds well with that of the microstructural change with  $P_{Nz}$ . The Fe-Hf-C-N films with 5%  $P_{Nz}$  exhibit effective permeability of about 2000 and saturation magnetization of 14 kG at as-deposited state, due to their high  $D_m$ . And the Fe-Hf-C-N films with over 3%  $P_{Nz}$  shows higher corrosion resistance than the N-free Fe-Hf-C films.

The present results indicates that the Fe-Hf-C-N films are considered to have high potentials for the head core materials suitable for high density recording systems, owing to their excellent soft magnetic properties and corrosion resistance as well as high saturation magnetization.

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