

RELATION BETWEEN MICROSTRUCTURE AND SOFT MAGNETIC PROPERTIES OF Fe-TM-C-N (TM:Hf, Zr AND Nb) NANOCRYSTALLINE FILMS

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Abstract The Fe-TM-C-N nanocrystalline films (TM : Hf, Zr and Nb) are investigated to examine the relation between microstructure and soft magnetic properties. In these films, as the atomic radius of TM element increases, P_{N_2} which was added to get good soft magnetic properties was decreased and the maximum value of the permeability shifted to the high Fe range in the composition diagram. The best soft magnetic properties achieved in these films are : H_c of 0.15 Oe, μ_{eff} of 7800 (1MHz) and $4\pi Ms$ of 17.5 kG in Fe-Hf-C-N film ; H_c of 0.06 Oe, μ_{eff} of 2750 (1MHz) and $4\pi Ms$ of 16.8 kG in Fe-Zr-C-N film and H_c of 0.31 Oe; μ_{eff} of 2100 (1MHz) and $4\pi Ms$ of 15.5 kG in Fe-Nb-C-N film. It was considered that the stronger the bonding force between TM and C(N), the finer TM(C,N) phase is precipitated and therefore, the finer α -Fe grains are formed. The effective permeability of the Fe-Zr-C-N films and Fe-Nb-C-N films remains nearly constant up to 10 MHz.

I. INTRODUCTION

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 high permeability materials have been directed to Fe-based nanocrystalline films[1]. It is so far reported that the addition of B, C or N elements or simultaneous addition of B and N, and N and O in Fe-TM (TM; transition metals such as Hf, Ta, Zr, etc.) is effective to improve soft magnetic properties and thermal stability[2]-[7].

The nanocrystalline films can be obtained by the crystallization of precursor amorphous films. TM-carbides or TM-nitrides formed during the heat treatment are considered to act as nucleation or pinning sites of grain growth. The decreased magnetocrystalline anisotropy of fine α -Fe grains is regarded as one of essential factors for magnetic softness[8],[9].

In this paper, we study the relation between structure and magnetic properties of Fe-TM-C-N films in order to better understand the mechanism responsible for the magnetic softness. A particular emphasis is given to see how the nanocrystalline structure is formed.

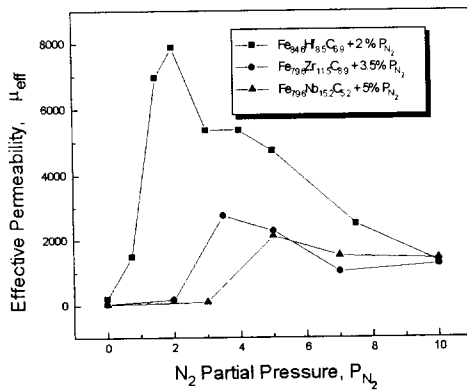
II. EXPERIMENTAL PROCEDURE

Fe-TM-C-N films were fabricated in Ar+N₂ plasma by an rf magnetron sputtering apparatus. The target consisted of an Fe disc with 100 mm diameter and small pieces of TM and C. The partial pressure of N₂ gas (P_{N_2}) was controlled in the range of 0 ~ 10% keeping the total gas pressure of 1×10^{-3} Torr constant. The films which were deposited onto Corning 7059 glass substrates were disc-shaped with 10 mm in diameter and 1 μ m in thickness. The deposition rate was 470 ~ 620 $\text{\AA}/\text{min}$., mainly depending on (P_{N_2}) at the power density of 3.82 watts/cm². The films were annealed at 450 ~ 700 °C for 30 min in vacuum. The composition of films was analyzed by Auger electron spectroscopy(AES), and some of films also by Rutherford backscattering spectroscopy (RBS). The saturation magnetization ($4\pi Ms$) and coercive force (H_c) were measured by a vibrating sample magnetometer (VSM). The effective permeability (μ_{eff}) was measured by a impedance analyzer using a horse-shoe shaped ferrite core and also by a permeability measurement system using 8-figure coil method up to 100 MHz. The microstructure was investigated by transmission electron microscopy (TEM) and X-ray diffractometry (XRD).

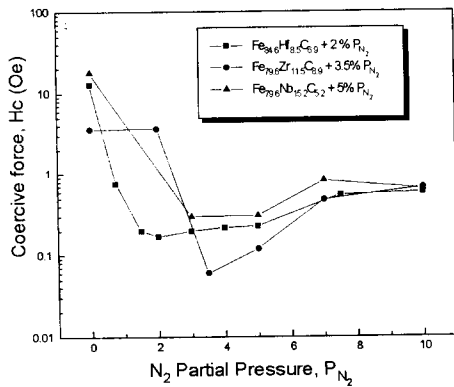
III. RESULTS AND DISCUSSIONS

Fig.1 shows the results for the effective permeability and the coercive force of Fe-TM-C-N films as a function of P_{N_2} . The permeability maximum shifts from 2% to 5% and the maximum value of the effective permeability decreases gradually as TM change from Hf to Nb. In these figures, we can see the dependencies of μ_{eff} and H_C on P_{N_2} for the Fe-TM-C-N films annealed at 550 °C. The films with 0% P_{N_2} indicate that the Fe-TM-C films were deposited in pure Ar plasma. The soft magnetic properties of the Fe-TM-C-N films are

influenced sensitively by the change of P_{N_2} . The μ_{eff} shows the peak value of 7800 at 2% P_{N_2} for the Fe-Hf-C-N films, 2750 at 3.5% P_{N_2} for the Fe-Zr-C-N films and 2100 at the 5% P_{N_2} for the Fe-Nb-C-N films. In the high P_{N_2} region over 7% P_{N_2} , μ_{eff} shows relatively low values. The H_C decreases abruptly with P_{N_2} , reaching a minimum value of about 0.15 Oe at 2% P_{N_2} for the Fe-Hf-C-N films, 0.06 Oe at 3.5% P_{N_2} for the Fe-Zr-C-N films and 0.31 Oe at the 5% P_{N_2} for the Fe-Nb-C-N films. And then increases with the further increase of P_{N_2} . As general phenomena in soft magnetic materials, this trend shows the reciprocal relation between the effective permeability and the coercive force.



(a)



(b)

Fig.1 The soft magnetic properties of the Fe-TM-C-N films annealed at 550 °C:(a) the effective permeability as a function of P_{N_2} (b) the coercive force as a function of P_{N_2}

Fig.2 shows TEM micrographs and electron diffraction patterns of $Fe_{84.6}Hf_{8.5}C_{6.9} + 2\% P_{N_2}$ film, $Fe_{79.6}Zr_{11.5}C_{8.9} + 3.5\% P_{N_2}$ film and $Fe_{79.6}Nb_{15.2}C_{5.2} + 5\% P_{N_2}$ film annealed at 550 °C. The films consisted of two phases; a fine crystalline α -Fe phase and dispersed TM(C,N) precipitates. The good soft magnetic properties of those nanocrystalline films are also believed to be due to the fact that the finely dispersed TM(C,N) precipitates which are normally formed at an early stage of crystallization suppress the growth of α -Fe grains. The amount of adding N_2 gas shows increasing tendency by the order of Hf, Zr and Nb. Though we cannot distinguish the grain size of the films accurately, we guess that the grain size of the Fe-Hf-C-N film is smallest among them and that of the Fe-Nb-C-N film is largest. It is considered as follows. As shown Table 1, the atomic radius of Hf is largest among them, the next is Zr. In case of Nb, the atomic radius is smallest among them. Therefore, if Hf is added to the matrix very small amount, the amorphous phase is formed easily. So, in Fe-Hf-C-N films, it is easy to form amorphous phase in low partial N_2 pressure.

To explain the formation of fine grain structure of the Fe-TM-C-N films, Fig. 3 shows the schematic diagram for the Fe-TM-C-N films. In Fe-TM-C films, we get the nanocrystalline films with good magnetic properties by crystallization of homogeneous amorphous phase. It is considered that the TM-C precipitates formed in

Table 1 The atomic radius size and amorphous forming abilities

Element	Periodic Table	Atomic Radius(A)	Amorphous Forming Ability(Fe-TM)
	Group Period		
Hf	IVa 3	1.67	Strong
Zr	IVa 2	1.58	Strong
Nb	Va 2	1.46	Medium

annealing suppress the grain growth after crystallization of α -Fe phase. But, in the Fe-TM-C-N films which were fabricated by N_2 reactive sputtering method, we considered that the mixture of amorphous phase and nanocrystalline was formed in as-sputtered state.

Fig. 4 shows the contour of μ_{eff} and $4\pi M_s$ in the Gibbs triangle for Fe-TM-C-N films annealed at 550 °C. The composition range in which good soft magnetic properties are obtained shifts from near Fe side to far away in the order of the Fe-Hf-C-N films, the Fe-Zr-C-N films and the Fe-Nb-C-N films. These results are expected if we consider the results mentioned previously.

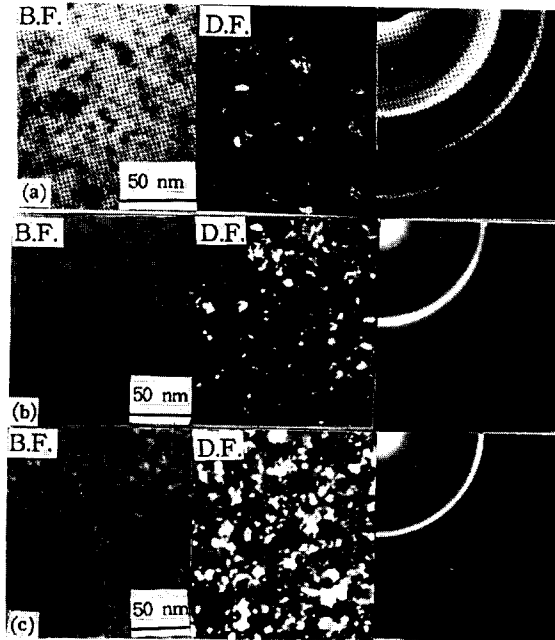


Fig. 2 TEM micrographs and diffraction patterns of Fe-TM-C-N films annealed at 550 °C; (a) $Fe_{84.6}Hf_{8.5}C_{6.9} + 2\% P_{N_2}$ film (b) $Fe_{79.6}Zr_{11.5}C_{8.9} + 3.5\% P_{N_2}$ film (c) $Fe_{79.6}Nb_{15.2}C_{5.2} + 5\% P_{N_2}$ film

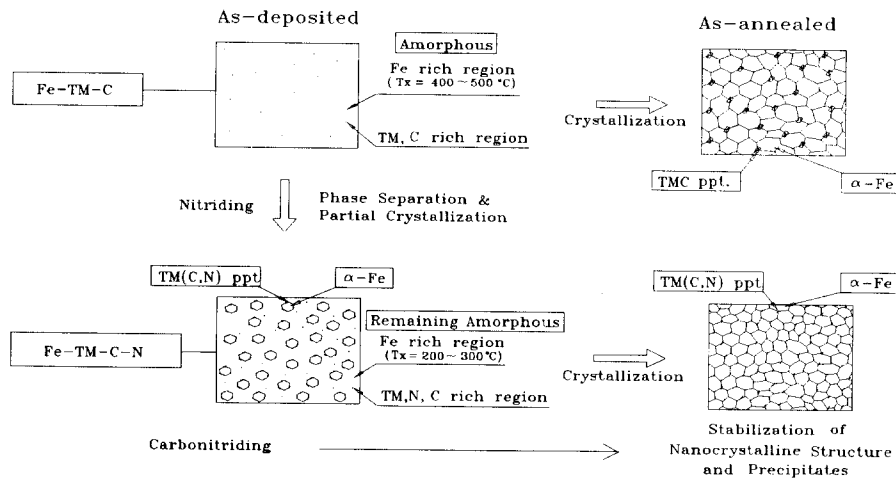


Fig. 3 Schematic diagram showing the formation of fine grain structure of the Fe-TM-C-N films

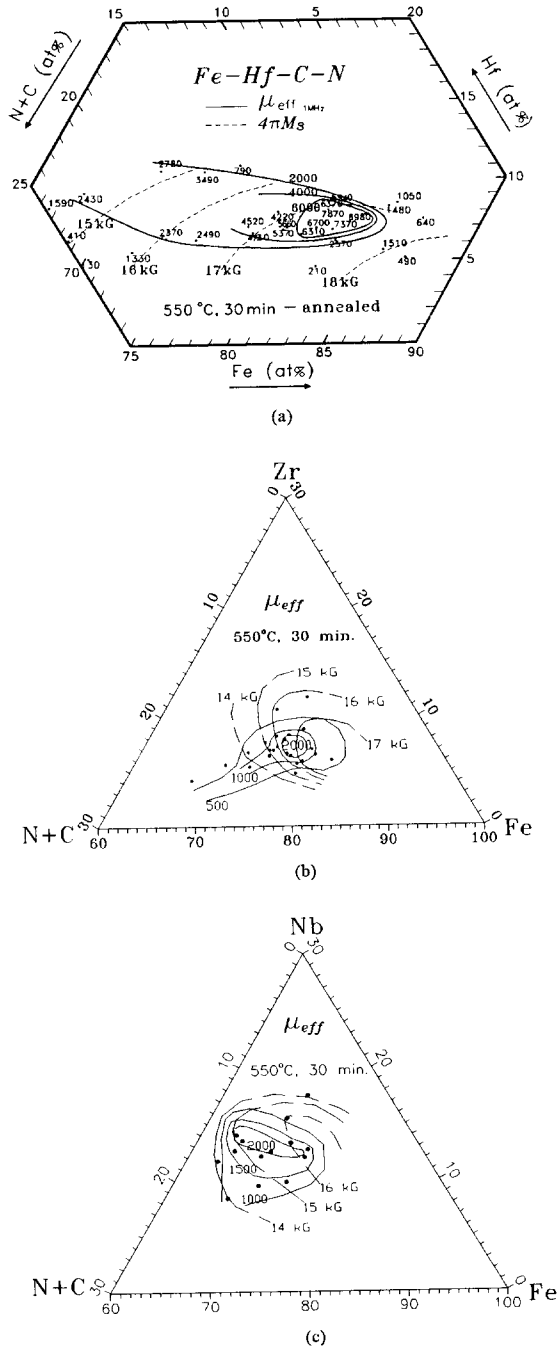


Fig. 4 The effective permeability and saturation magnetization of the Fe-TM-C-N films annealed at 550°C as a function of the composition; (a) the Fe-Hf-C-N films (b) the Fe-Zr-C-N films (c) the Fe-Nb-C-N films

Fig. 5 shows the dependence of the effective permeability on the frequency. The effective permeability of Fe-Zr-C-N and Fe-Nb-C-N film are hardly deteriorated up to 10 MHz. In high frequency region, the eddy current loss is a main factor of decreasing effective permeability. The eddy current loss is decreased as resistivity is increased. In the case of the Fe-Nb-C-N films, the resistivity was increased from 91 $\mu\Omega\cdot\text{cm}$ for 0% P_{N_2} to 167 $\mu\Omega\cdot\text{cm}$ for 5% P_{N_2} . Therefore, it is considered that the resistivity of films increased because of N_2 addition.

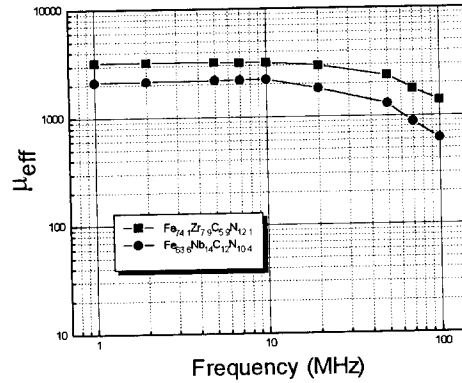


Fig. 5 Dependence of effective permeability on the frequency in Fe-TM-C-N (TM:Zr, Nb) films

To discuss the differences of magnetic properties such as $4\pi M_s$, μ_{eff} and H_c in Fe-Zr-C-N and Fe-Nb-C-N films, the composition and the best magnetic properties are listed in Table 2 together with those of Fe-Hf-C-N films.

The $4\pi M_s$ and maximum μ_{eff} of three films decrease in the order of 17.5 kG (Hf) > 16.8 kG (Zr) > 15.5 kG (Nb) and 7800 (Hf) > 2750 (Zr) > 2100 (Nb), respectively. These tendencies correspond well to the magnitudes of the formation enthalpy which are in the order of Hf(C,N) > Zr(C,N) > Nb(C,N). The stronger the bonding force between TM and C(N), the finer the TM(C,N) precipitates will be and therefore, the finer α -Fe grains will be formed.

Table 2 The composition and the soft magnetic properties of Fe-TM-C-N films and the formation enthalpies of TM-C and TM-N

	Fe-Nb-C-N	Fe-Zr-C-N	Fe-Hf-C-N
Composition	Fe _{83.6} Nb ₁₄ C ₁₂ N _{10.4}	Fe _{74.1} Zr _{7.9} C _{5.9} N _{12.1}	Fe _{81.4} Hf _{8.2} C _{6.7} N _{3.7}
4 π Ms (kG)	15.5	16.8	17.5
μ_{eff} (at 1 MHz)	2100	2750	7800
Hc (Oe)	0.31	0.06	0.15
ΔH_{1298} of TM-C (kJ/mol)	-139	-197	-251
ΔH_{1298} of TM-N (kJ/mol)	-235	-365	-374

IV. CONCLUSIONS

We studied the relations between microstructure and soft magnetic properties of Fe-TM-C-N(TM: Hf, Zr, Nb) films. The fine grained α -Fe structure, together with finely dispersed TM(C,N) precipitates which formed at an early stage of crystallization is considered to be one of the main factors for the good magnetic properties in Fe-TM-C-N films. It was considered that the difference of the formation enthalpy between TM element and carbon/nitrogen caused the difference of the magnetic properties of the Fe-TM-C-N films. Taking into consideration of the frequency stability for the effective permeability, the Fe-Zr-C-N films as well as the Fe-Nb-C-N films are estimated as the proper head core

materials used in high frequency region. The best soft magnetic properties achieved in these films are; Hc of 0.15 Oe, μ_{eff} of 7800 (1MHz) and 4π Ms of 17.5 kG in Fe-Hf-C-N film, Hc of 0.06 Oe, μ_{eff} of 2750 (1MHz) and 4π Ms of 16.8 kG in Fe-Zr-C-N film and Hc of 0.31 Oe, μ_{eff} of 2100 (1MHz) and 4π Ms of 15.5 kG in Fe-Nb-C-N film.

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