CHANGES OF MAGNETIZATION AND MICROTEXTURE OF NICKEL CLUSTERS IN POLYIMIDE FILM BY HEAT TREATMENT

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Introduction

Recently, we prepared a Kapton type polyimide film containing Ni with about 50 μm in thickness by mixing $Ni(NO_3)_2$ with polyamic acid (PAA: poly 4,4'-oxydiphenylene pyromelitamic acid) in solution and by following imidization at 200℃ on a glass plate. The structure, texture and magnetization of the polyimide film (PIF-$Ni(NO_3)_2$) and carbonized ones were studied[1,2]. However, the change of magnetic property during carbonization of PIF-$Ni(NO_3)_2$ has not been examined enough. In the present study, magnetization of PIF-$Ni(NO_3)_2$ and the heat-treated ones used in Refs. 1 and 2 was measured in detail, and change of magnetic property due to Ni clusters formed in the film with heat treatment was investigated in relation to the sizes of the Ni clusters.

Experimental

The methods of preparation and heat treatment of PIF-$Ni(NO_3)_2$ were given in Ref. 1. The weight ratio of Ni in $Ni(NO_3)_2$ to PAA was 3.9wt%. The heat-treated film is named hereafter PIF-Ni followed by the heat treatment temperature (HTT). The contents of Ni in PIF-Ni200 - 900 were estimated by x-ray fluorescence spectroscopy for PIF-Ni600 and 800, and from weight loss during heat treatment. The value of Ni content w_{Ni} for each sample is listed in Table 1. Average crystallite size L_{111} of Ni clusters was determined from (111) peak of Ni by x-ray diffraction. Microtexture of surfaces and cross sections of PIF-Ni400 - 900 was observed using a field emission gun type scanning electron microscope (FESEM). Mass magnetization was measured as a function of magnetic field in fields up to ± 50000Oe applied parallel to each film surface, and as a function of temperature in the range 2 - 280K using a SQUID magnetometer. Kapton type polyimide films without Ni were also prepared and heat-treated in the same HTT range. Mass magnetization M was measured for them in the same condition in order to check the magnetization due to polyimide and carbon matrix.

Results and discussion

From the FESEM photographs, the range of diameter D of visible clusters of Ni or Ni compounds (D>5nm) in PIF-Ni450 - 900 was estimated as listed in Table 1. D for PIF-Ni400 was obtained by TEM. The clusters are formed during decomposition of PIF-Ni, and increase in size by carbonization above 700℃. It is noted that fine clusters with D = 5 - 10nm exist in PIF-Ni heat-treated at any temperature up to 900℃. The clusters in PIF-Ni400 - 500 are considered to be Ni compounds such as NiO and Ni_3C.

PIF-Ni and PIF-Ni300 exhibit Curie type paramagnetic behavior at low fields in the temperature dependence of mass magnetization. The temperature dependence of zero field cooled magnetization M_{ZFC} and field cooled magnetization M_{FC} of 80 Oe is shown in Fig. 1. For PIF-Ni200(original) and 300, M_{ZFC} coincides with M_{FC}, while an irreversible effect is observed below a critical temperature T_F for PIF-Ni350 - 900. This irreversible effect arises from the freezing of spin directions of ferromagnetic Ni clusters at temperatures below T_F. T_F tends to be increase with increasing HTT, indicating the increase of Ni cluster size.

Figure 2 shows M as a function of magnetic field H at temperatures of 5 and 280K. PIF-Ni samples heat-treated above 400℃ exhibit ferromagnetic behavior, and hysteresis loops were observed. Total magnetic moment M_0 of ferromagnetic component in each sample is evaluated from the linear extrapolation of M in high field region (H>20kOe) to 0Oe at 280K. The Ni content W_{Ni} (wt%) of ferromagnetic component in each sample is estimated from M_0 using the values of atomic magnetic moment of bulk Ni (5.71×10^{-21}emu) and mass of Ni atom (9.75×10^{-23}g). The superparamagnetic component was obtained by subtracting the background magnetism of polyimide and/or carbon matrix and the ferromagnetic component from M. Mean magnetic moment m of one superparamagnetic Ni cluster and total magnetic moment $N \cdot m$ of superparamagnetic component in each sample were evaluated by fitting the obtained superparamagnetic component to the Langevin function. Then, the number of superparamagnetic Ni clusters N is obtained from $N \cdot m$ and m. The values of M_0, W_{Ni}, $N \cdot m$ and N thus obtained are listed in Table 1. The changes of these values by HTT explain well the change of cluster sizes of Ni and Ni compounds evaluated from X-ray

diffraction and FESEM.

References

1. Kaburagi Y, Hishiyama Y and Hatori H, Magnetic property of a polyimide film containing small amount of fine nickel particles and the carbonization effect. Extended Abstracts, 24th meeting of Japanese carbon society, Ehime (Japan): 1997; 80-81.
2. Yoshida A, Kaburagi Y, Hishiyama Y and Hatori H, Textural change in nickel-containing polyimide films with carbonization. Extended abstracts, Eurocarbon'98, Strasbourg (France): CAKK and GFEC, 1998; 785-786.

Acknowledgment

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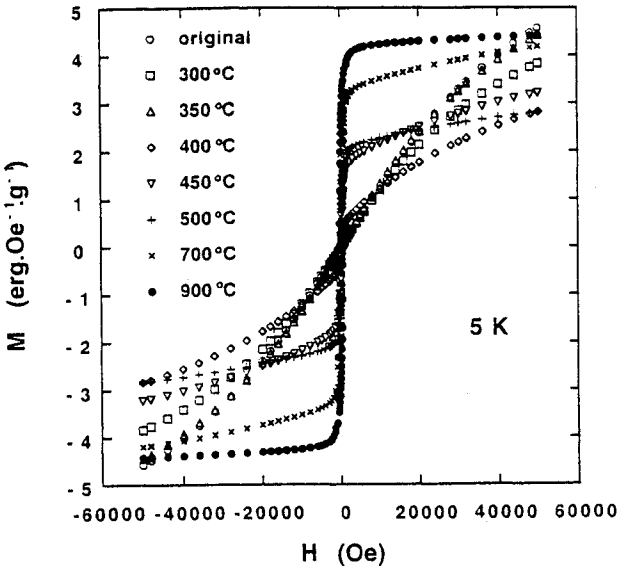

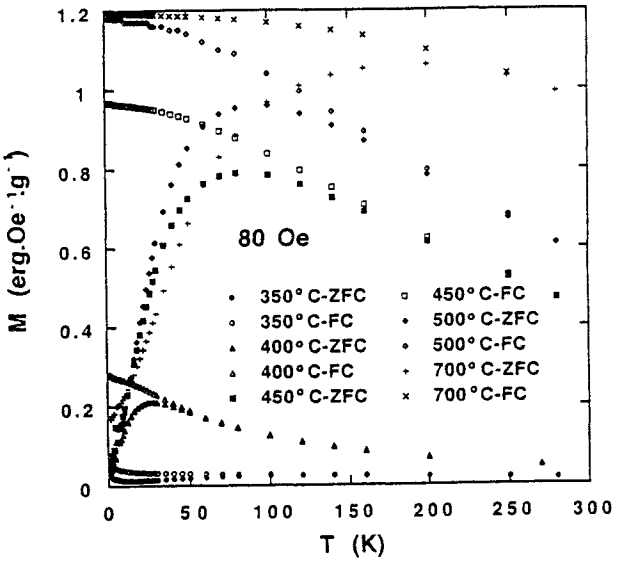

Fig. 1. Temperature dependence of zero field cooled magnetization M_{ZFC} and field cooled M_{FC} of 80 Oe.

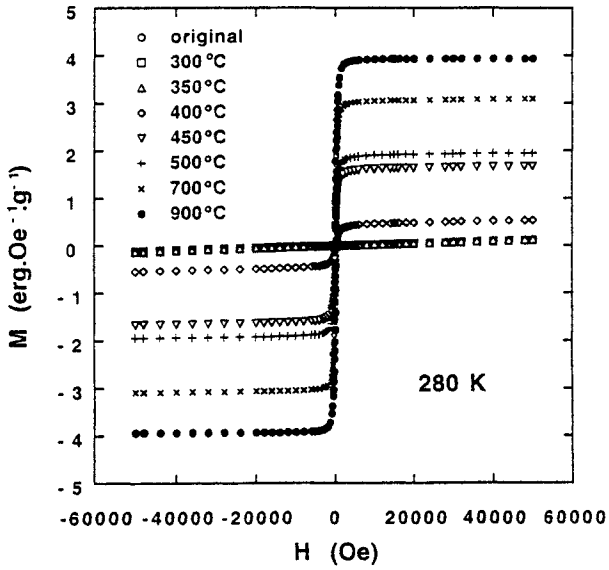

Fig. 2. Mass magnetization as a function of magnetic field at temperatures of 5 and 280K.

Table 1. Values of w_{Ni}, L_{111}, D, M_0, W_{Ni}, $N \cdot m$ and N for PIF-Ni$(NO_3)_2$ and heat-treated samples.

HTT(℃)	200	300	350	400	450	500	600	700	800	900
w_{Ni} (wt%)	4.4	5.1	5.2	6.0	7.2	7.5	8.1	8.5	9.9	10.3
L_{111} (nm)	---	---	---	---	6.9	8.2	9.3	19.1	25.6	25.8
D (nm)	---	---	---	(3~15)	20~25	20~25	5~10	5~50	10~80	10~130
M_0 (emu/g)	0.00	0.00	0.00	0.48	1.72	2.03	---	3.25	---	4.19
W_{Ni} (Wt%)	0.00	0.00	0.00	0.83	2.49	3.47	---	5.54	---	7.15
$N \cdot m$ (emu/g)	6.7	5.9	6.4	3.2	2.2	---	---	1.1	---	0.19
N (N/g) x10^{-20}	1.6	1.5	1.4	0.84	0.69	---	---	0.35	---	0.043