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ABSTRACT

In a wide range of composition Gd-Fe thin films become amorphous. The diffraction patterns of diffuse halo rings are distinguished into three types. The type 1 with a single strong halo appears in the 30-60 percent iron films of any thickness. The type 2 with two strong halos of nearly the same intensity and the type 3 with two halos of different intensities appears in the 60-90 percent iron films thicker and thinner than about 100 A, respectively. Within one type of pattern the peak position of halos shifts with the variation of composition and thickness of the film. The type 2 pattern can be well correlated to the diffraction pattern of the intermetallic compound Fe_3Gd with a rhombohedral structure. The other patterns are difficult to relate with a special type of crystalline phase.

INTRODUCTION

Combination of many rare earth and 3d transition metals (RE-TM) is known to be made amorphous alloys by suitable preparation methods such as vacuum deposition (1), sputtering (2), etc. The atomic arrangement that depends on preparation and treatment of an amorphous film is considered to effect largely to the structure sensitive magnetic property. In order to prepare amorphous films with controlled properties information on amorphous state of this system itself becomes important.

Electron diffraction is one of the most sensitive method to investigate amorphous state of a thin film, though numerical accuracy may be lower than X-ray diffraction. There is another benefit; high resolution electron microscopic images can be observed at the same time, which helps understanding of the film structure.

Amorphous Gd-Fe films have always been discussed in comparison to amorphous Gd-Co films which have been the one of the most intensely investigated system due to application possibility to the bubble domain material. Recently, several RE-Fe combinations attract attention as the magneto-optical and thermo-magnetic recording material (3,4).

EXPERIMENTAL

Gadolinium, iron and their alloys with compositions from 40 to 90 atomic percent iron were prepared to buttons of about 5 mm in diameter being melted from pure metals by electron beam in vacuum. The button was heated by one electron beam in an ordinary vacuum apparatus with liquid nitrogen trap, and pure metal or alloy films were deposited on thin amorphous carbon films spread on copper grids for electron microscopy at liquid nitrogen temperature. The vacuum during the deposition was among 5×10^{-6} to 1×10^{-7} torr. At the same time the films for the thickness, composition and magnetic measurements were prepared on glass substrates also cooled by liquid nitrogen.

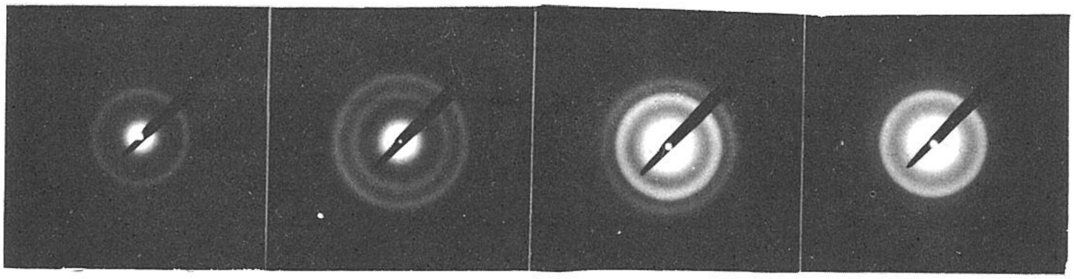
The thickness was determined by a multiple interference method. The composition was determined by electron probe microanalysis with atmost care. The magnetic moment was measured by magnetic balance. Soon after the deposited film was warmed to the room temperature, the sample was removed from the vacuum chamber to a 100 kV transmission electron microscope to observe the electron diffraction pattern, the high resolution image and the magnetic domain pattern by Lorentz microscopy. Each film was examined several times with an interval from several days to six months,being kept in an ordinary desiccator. Some of photographic films of the electron diffraction patterns were traced by a microdensitometer.

RESULTS

The alloy films prepared by thirty times of different runs cover sufficiently wide range of compositions from 30 to 90 atomic percent iron. The composition of the deposited film is always much more iron rich than the mother alloy in spite of the higher vapour pressure of gadolinium than iron at any temperature above the melting point. The composition noted is the analysed value. The thickness is between 300 and 1200 A but every film includes small area of very thin parts due to the shadowing effect by the edge of copper grid or depressions of the substrate carbon film.

The Gd-Fe film with a composition between 0 and 35 percent iron, and 90 and 100 percent iron is crystalline state with well defined diffraction rings up to higher orders of indices. All the films with the intermediate compositions show diffuse halo patterns in electron diffraction. Any coherent image can not be recognized by high resolution electron microscopy of the film with the diffuse halo diffraction pattern, while the film with distinct crystallites shows clear diffraction rings. The difference between the halo pattern and the ring patterns from very small polycrystalline phase can not be mixed. There is no remarkable difference between the patterns of each film observed soon after deposition and after six months. In this report such film as its diffraction pattern shows halo rings only is called amorphous.

Three different halo patterns, type 1,2 and 3, are recognized. Typical ones are shown in Fig.1. The pattern varies with the composition and the thickness of the film.



a b c d

Fig.1 Typical diffraction patterns of deposited Gd-Fe films.
a: the type 1 (a $Gd_{57}Fe_{43}$ film of 360 A),
b: the type 2 (a $Gd_{17}Fe_{83}$ film of 540 A),
c: an intermediate state between the type 2 and 3,
d: the type 3 (a $Gd_{17}Fe_{83}$ film of 100 A).

The type 1 consists of a single strong inner halo and one or two more very weak halos as shown in Fig.1-a for the 360 A film of $Gd_{57}Fe_{43}$. That is a typical halo pattern of a so called amorphous film. This type of pattern appears in the Gd-Fe films with 30 to 60 percent iron of any thickness examined.

The type 2 consists of two strong inner halos with nearly the same intensity and two or three more weak halo rings outside of them as shown in Fig.1-b for the 540 A film of $Gd_{17}Fe_{83}$. The type 3 also consists of two inner halos but the intensity of the first is much stronger than the other as shown in Fig.1-d for the very thin part of $Gd_{17}Fe_{83}$ film. The type 2 and 3 always appear in a different parts with different values of thickness of the same film and corresponds to thicker and thinner part, respectively. The boundary thickness is estimated to lie around 100 A. The composition range for these types is 60 to 90 percent iron. The relation between the composition of alloy and the diffraction pattern is listed in Table 1 together with specific compositions in the phase diagram of Gd-Fe system (5).

Table 1 Composition dependence of the diffraction patterns of the deposited Gd-Fe films at liquid nitrogen temperature.

% Gd	100	90	80	70	60	50	40	30	20	10	0
% Fe	0	10	20	30	40	50	60	70	80	90	100
Crystalline phase	—	—	—	—						—	—
Amorphous phase											
Type 1				—	—	—	—				
Type 2							—	—	—	—	
				eutectic point				Fe_2Gd	Fe_3Gd		

Microdensitometric traces of the patterns in Fig.1 are shown in Fig.2 in order to compare the relation of each pattern, where the ordinate shows the diffracted intensity in arbitrary unit and the subordinate is the scattering vector $S = 4\pi \sin\theta/\lambda$ in A^{-1} unit.

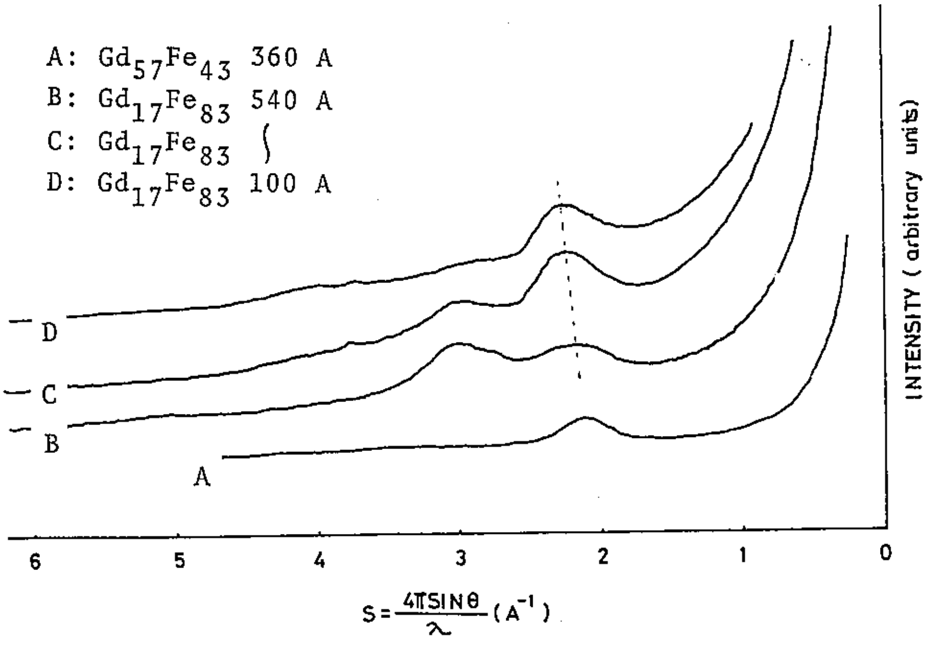


Fig.2 The microdensitometric traces of the diffraction patterns shown in Fig.1.

Though the same type of pattern appears for a wide range of composition, the central position of halo varies with composition and thickness. The position of the peak 1, P_1, of the type 2 pattern shifts toward smaller S value with the decrease of iron content to coincide with the peak 1 of the type 1 pattern at a gadolinium rich film. P_1 shifts toward larger S with the decrease of thickness to coincide with the peak 1 of the type 3 pattern at sufficiently small thickness. The position of the peak 2, P_2, of the type 2 pattern shifts toward larger S with the increase of iron content and disappears at gadolinium rich films. P_2 shifts toward smaller S with the decrease of thickness and at the same time the intensity of P_2 decreases. The intensity of the halos moves gradually between the type 2 and 3 patterns when only the thickness varies.

The observed range of peak shifts with composition are listed in Table 2 together with the calculated peak positions

Table 2 The peak position of halos.

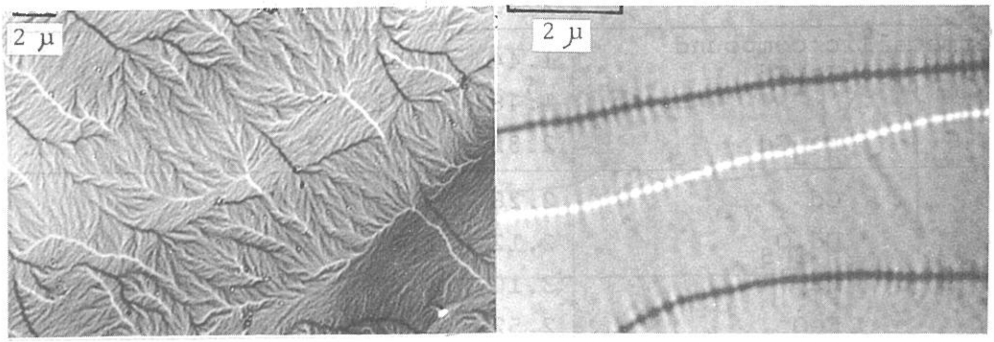
$S = 4\pi\sin\theta/\lambda$ A^{-1}	P_1	P_2	P_3	P_4	P_5
Crystalline $Fe_{35}Gd_{65}$ film	2.08	2.20	3.30	4.00	
Gd-rich ↑ Amorphous Fe-Gd film ↓ Fe-rich — Type 1	2.08 ~ 2.15				
Type 2	2.00 ~ 2.45	2.93 ~ 3.33	3.85 ~ 4.24		
Intermetallic compound Fe_2Gd	1.44 ~ 1.48	1.67 ~ 1.71	2.36 ~ 2.42	2.77 ~ 2.83	
Fe_3Gd	2.32	2.96	3.16	3.57	4.25
Gd	2.28	3.47	4.08		
Gd_2O_3	2.12	2.23	2.29		
Fe	3.10	4.39	5.58		
FeO	2.52	2.92	4.13		
α-Fe_2O_3	2.33	2.50	3.72		
γ-Fe_2O_3	2.13	2.49	4.25		
Fe_3O_4	2.48	3.90	4.25		

of diffracted lines for some intermetallic compounds of the Gd-Fe system and those of oxides of iron and gadolinium. The lattice parameters reported by different authors scatter considerably. The most reliable values are adopted for Fe_3Gd of a rhombohedral structure and the values from the maximum to the minimum are used for Fe_2Gd of a face centered cubic structure (5).

DISCUSSION

It is clearly seen from Table 2 that the three peaks of Gd_2O_3 are included in the intensity of the halo peak P_1 if such an oxide is produced. However, there is a problem whether the observed diffraction patterns are those of the amorphous Gd-Fe films or of the oxides.

Unless the Gd-Fe films are prepared at a ultra-high vacuum and examined in-site electron microscopy, oxidation of the thin film sample is inevitable because gadolinium metal is easy to oxidize. Since there is not magnetic interaction between gadolinium and oxygen, only metallic phase contributes to the ferrimagnetic moment. The electron microscopic sample exhibits magnetic domain patterns in Lorentz microscopy as shown in Fig.3 for the same films to Fig.1, $Gd_{57}Fe_{43}$ and $Gd_{17}Fe_{83}$, and



a b

Fig.3 Domain patterns of the same films shown in Fig.1.
a: the $Gd_{57}Fe_{43}$ film of 360 A,
b: the $Gd_{17}Fe_{83}$ film of 540 A.

proves itself to be ferromagnetic (ferrimagnetic), that is, the film is composed of considerable layers of metallic phase.

Another problem is whether oxygen and metal atoms are mixed as uniform layers of amorphous state, or gadolinium atoms are oxidized selectively leaving metallic iron atoms.

If iron atom only contributes to the magnetic moment of the Gd-Fe films, the composition dependence of the magnetic moment should be monotonous one with the increase of iron content. Experimentally, the composition dependence of the magnetic moment of the Gd-Fe films shows the minimum at the compensation composition, which means that iron and gadolinium atoms interact ferrimagnetically through the composition range. Then, large parts of the diffraction intensity that varies with composition comes from the metallic amorphous phase, though there may be some contribution from the oxides.

The phenomena on amorphous Gd-Fe alloy films can be separated into three parts. First, there are different state of amorphous phases within a system of deposited Gd-Fe films depending on the composition. Second, there is a composition range where the amorphous structure changes from one of thick thin films to another of the very thin films. Third, short range orders of some amorphous structure resemble to that of a crystalline phase.

As several intermetallic compounds are formed peritectically in many RE-TM systems, the RE-TM alloys are easy to become amorphous in a wide range of composition. Considering similarity in those systems it may be expected that the composition depending variation in amorphous state within one system as shown for the deposited Gd-Fe films is common to them though it has not been reported yet for a similar system.

Thickness dependence of the halo position is reported on the sputtered Gd-Co films with cobalt rich compositions (6). The tendency of the peak shift of these Gd-Fe films is similar to that of Gd-Co, but there is difference in experimental details. At the same time, only by the number of Gd-O pairs as explained in the case of the Gd-Co films is insufficient to understand why there is not such a thickness dependence in the gadolinium rich Gd-Fe films. Further investigation is needed.

The diffraction pattern similar to the type 2 is reported for Gd-Co films (7,8). In both cases the Gd-Co films of cobalt rich compositions show microstructure in electron micrograph and the splitting of halo peak becomes distinct with the heat treatment. Here it is noticed that each set of peaks in the type 2 pattern of the amorphous Gd-Fe films and those of the crystalline rhombohedral compound, Fe_3Gd, resembles to each other. At the same time, the composition range where the type 2 pattern appears is also around that of the compound. So long as deduced from the comparison of Table 2 there is possibility that the explanation with microcrystallite of cobalt or gadolinium and cobalt compounds in the case of Gd-Co system can be replaced by that with the compound of iron and gadolinium in the Gd-Fe system. On the other hand, corresponding microstructure is not observed in those as-deposited films. There may be an amorphous phase with a short range order like some ordered phase for a special ratio of two kinds of atoms.

CONCLUSION

In a wide range of composition amorphous Gd-Fe films were prepared by vacuum deposition at liquid nitrogen temperature and the composition and thickness dependence of the electron diffraction patterns were observed. Three types of halo patterns are distinguished.

The type 1 consists of a single strong halo and one or more very weak halos, and appears in the 30-60 percent iron Gd-Fe films of any thickness. The type 2 consists of two strong inner halos with the nearly same intensity and two or three more weak halos outside of them, while the type 3 consists of two inner halos also but the inner halo is much stronger than the other. The type 2 and 3 appear in the 60-90 percent iron Gd-Fe films of thicker and thinner than about 100 A, respectively.

Within one type of pattern the peak position of halos shifts with the variation of the composition and the thickness. The peak positions of the type 2 pattern can be related to those of the crystalline Fe_3Gd with a rhombohedral structure. The phenomena can not be explained by the reported results of detailed analysis for Gd-Co films.

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