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Structure formation in Gd–Fe thin films

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Abstract

The structure, thermal stability and kinetics of phase transformations were explored for films of Gd_2Fe_{17} compounds. The films were obtained by means of thermal evaporation in vacuum. Amorphous films were found to form at room temperature of substrates, amorphous-crystal condensates at $T_s = 300$–500 K, and polycrystalline films at $T_s > 500$ K. The crystal structure of condensates was determined at various temperatures and crystallization of amorphous films was found to be heterogeneous in character. Two phases, Gd_6Fe_{23} and a-Fe, were observed in polycrystalline films, while three phases were found to exist in the films obtained at substrate temperatures >500 K: a hexagonal Gd_2Fe_{17} phase of the Th_2Ni_{17} structural type, a rhombohedral Gd_2Fe_{17} phase of the Th_2Zn_{17} structural type and a hexagonal $GdFe_5$ phase of the $CaCu_5$ structural type.

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1. Introduction

The interest in structural studies of Gd_2Fe_{17} films is mostly due to their peculiarity among compounds of the 'rare earth metal–iron' type, consisting in the coexistence in equilibrium of two phases of different structure but close to Gd_2Fe_{17} in composition [1]. One of these phases exists at an excess, the other at a deficiency of Fe. Their coexistence has caused a diversity of processes in films' structure and substructure formation, depending on the technological conditions of precipitation. The purpose of this paper is to investigate the kinetics of phase changes during thermal annealing and to establish the connection between the structure of the formed films and the temperature of substrates as a technological parameter.

2. Experimental procedures

Films of the Gd_2Fe_{17} compound were obtained by techniques of thermal evaporation in vacuum of polycrystalline stock composed of Gd_2Fe_{17}. For structural investigations, 500–600 A thick films were precipitated on chips of alkali-haloid monocrystals (NaCl and KCl). The films' thickness was defined by means of an optical interferometer. The substrate temperature was set at 300–500 K. The structural investigations were carried out by an UEMV-100K electron microscope. The thermal stability and kinetics of crystallization of amorphous Gd_2Fe_{17} films were investigated by means of direct heating inside the microscope's column (heating rate 5–30 K/min). During this process, the temperature of emergence of the most intensive diffraction peaks was detected in the background of a diffuse 'halo'. This temperature corresponds to the beginning of the crystal phase's generation.

3. Results and discussion

An electronographic investigation of films precipitated at $T_s = 300$ K on a polycrystalline NaCl substrate have shown amorphous condensates to form under these conditions (Fig. 1). Amorphous films are distinguished by a high level of structural disorder and appear to be meta-stable. During heating, the energy of amorphous film initially

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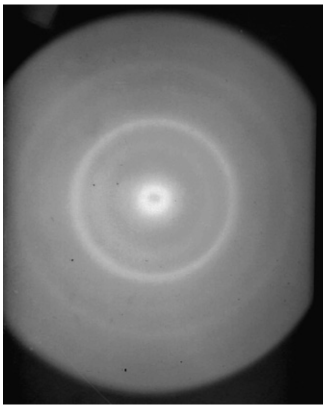

Fig. 1. Electronogram for amorphous Gd_2Fe_{17} films, obtained at $T_s = 300$ K (T_s – substrate temperature).

decreases as a result of relaxation into a more stable state within the amorphous phase and crystallization is observed at higher temperatures only [2].

An analysis of crystallization kinetics (Fig. 2) has proved the initial crystallization phase to consist of a-Fe crystallites. At this stage, the most intensive diffraction maxima of a-Fe have been detected in the background of a 'halo', corresponding to interplanar distances of $d_{110} =$ 2.02 A, $d_{200} = 1.43$ A, $d_{211} = 1.17$ A, $d_{310} =$ 0.91 A (Fig. 2b).

Fluctuations in the chemical composition of Gd_2Fe_{17} condensates appear to occur during precipitation on cold substrates; there are regions enriched with Fe and those depleted of Fe [3].

An inhomogeneity of chemical composition in the amorphous state offers a possibility to govern the formation process of fine-dispersed a-Fe crystallites in an amorphous matrix. a-Fe crystallites grow in a matrix so that no preferred orientation can be observed in electronograms. During this process the a-Fe crystallites transfer their the surplus of Gd to the surrounding amorphous matrix. The seed density for a-Fe phases depends on the continuous heating rate of the amorphous film (it increases at an increased rate).

The size of a-Fe crystallites increases with temperature growth, as indicated by decreased half-width of diffraction lines in electronograms and estimates of crystallite size directly on images taken from the electronic microscope. At increased temperature ($T > 600$ K), crystallization of the Gd-enriched amorphous matrix begins along with the formation of crystallites of Gd_6Fe_{23} compounds (structural type Gd_6Fe_{23} with space group Fm-3 m). This is indicated by the most intensive diffraction lines of this phase, $d_{422} = 2.47$ A, $d_{333} = 2.33$ A, $d_{440} = 2.14$ A, appearing in the electronograms (Fig. 2c).

The process of crystallization of amorphous films is completed with the formation of polycrystal films with a-Fe and Gd_6Fe_{23} phases. The appearance of Gd_6Fe_{23} should be surprising since this compound is one of the most stable in the Gd–Fe system [4,5]. The Gd_6Fe_{23} phase is always present in Gd–Fe systems, even in their massive state, during attempts to synthesize a compound with abundance of Fe ($GdFe_5$, Gd_2Fe_{17}) without special techniques.

A substantially different picture can be seen in the kinetics of phase formation during precipitation of Gd_2Fe_{17} films on pre-heated substrates. At temperatures ranging from room temperature to $T_s = 400$ K, amorphous films are generated. At $T_s = 500$ K, the films become amorphous-crystalline. With T_s rising further, the fraction of the polycrystalline phase increases. An analysis of electronograms (Table 1) has shown that the polycrystalline part of films consists of three phases: a hexagonal Gd_2Fe_{17} compound (60%) of the Th_2Ni_{17} structural type (φ_1 phase), a rhombohedral Gd_2Fe_{17} compound (30%) of the Th_2Zn_{17} structural type (φ_2 phase) and a small amount of a hexagonal $GdFe_5$ compound of the $CaCu_5$ structural type. An elementary lattice for modification of a Gd_2Fe_{17} compound constructed on the basis of diffraction data by means of a PowderCell computer code is presented in Fig. 3 ($a =$ 8.50 A, $c = 8.35$ A).

Compounds of the R_2Fe_{17} type (rare-earth metal and iron) are created in the range from Ce till Ho. In R_2Fe_{17} compounds (R: Ce, Pr, Nd, Sm, Gd), φ_2 phases form in equilibrium with RFe_5 compounds, but in R_2Fe_{17} compounds (R: Gd, Dy, Ho, Er, Tu, Yb, Lu) the φ_1 phase is formed in equilibrium with a-Fe [1]. The Gd_2Fe_{17} compound has a unique position, as it can be simultaneously formed both in φ_1 and in φ_2 phases. R_2Fe_{17}-type compounds belong to one of the phases depending on their ratio of atomic radiuses (r_R/r_{Fe}): at higher ratios φ_2-type phases are formed, at lower ones – the φ_1 phase, while at average values compounds of both types are formed (the Gd–Fe system).

The φ_1 phase differs from the φ_2 phase in composition. The former always appears at greater abundance of Fe in comparison to the latter. Thus, these phases do not appear to be polymorphic modifications of the same compound. The large values of lattice periods indicate that a_0 is always smaller in the φ_1 phase and the c_0/a_0 ratio is always comparatively greater than in the φ_2 phase, since the φ_1 phase has a higher level of substitution of R by Fe_2 than for the φ_2 phase.

In our case, the emergence of both phases in Gd_2Fe_{17} films indicates generation of micro-regions enriched with or depleted of iron. This mechanism of film formation leads to mutual blocking of crystallites' growth for φ_1 and φ_2 phases, which entails the possibility of the amorphous state in the Gd_2Fe_{17} inter-metallic compound and the high thermal stability of the amorphous state in films precipitated on substrates at room temperature. During precipitation of films on preheated substrates, the diffusion path of adatoms increases, with an accompanying decrease of seed density for the crystal structure of φ_1 and φ_2 phases [6]. The possibility of amorphous-crystal films forming already at $T_s = 500$ K suggests that the substructure, not the nature of chemical bounds between the components,

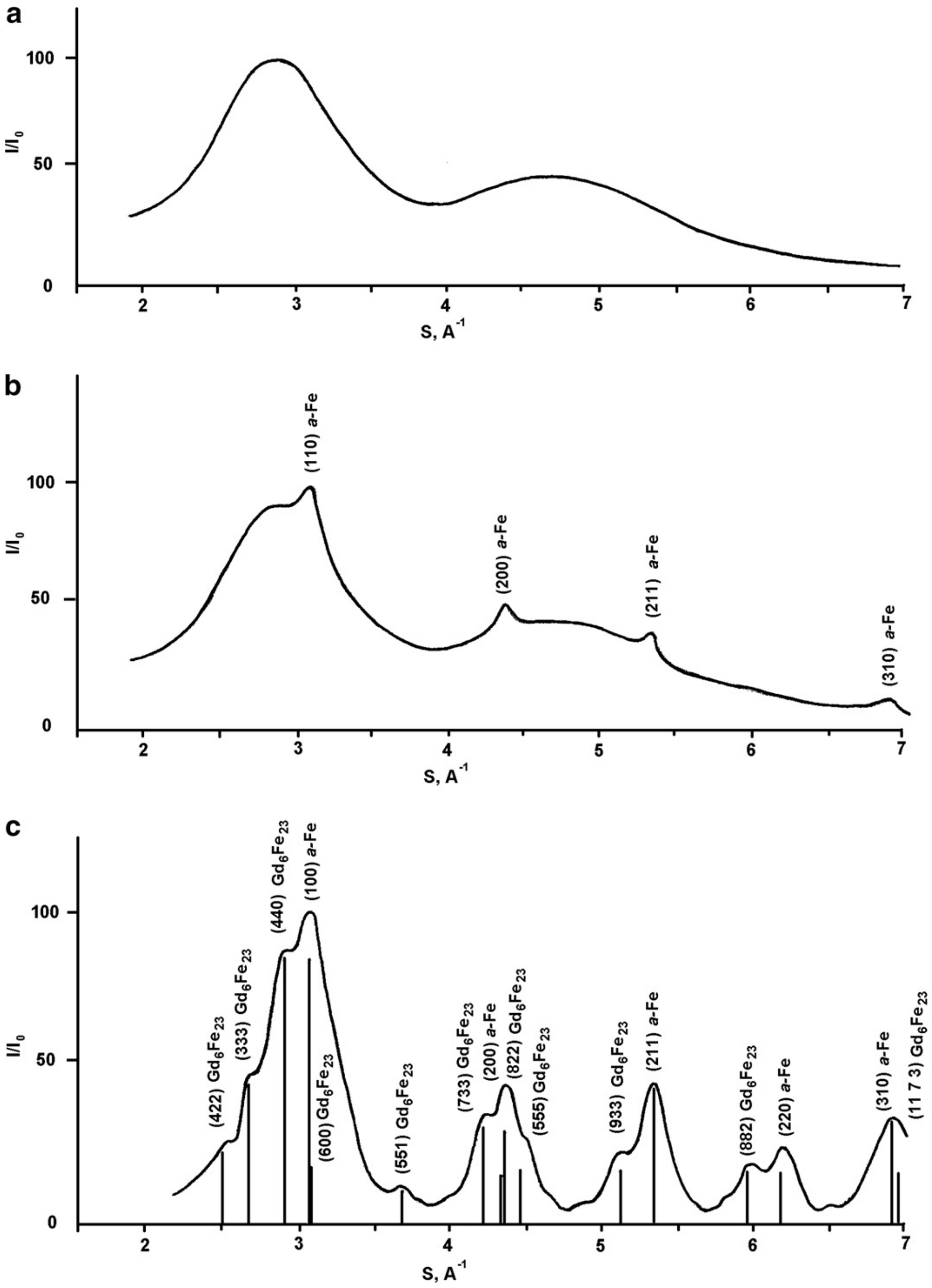

Fig. 2. Curves of electron scattering from Gd_2Fe_{17}films: (a) $T = 300$ K, (b) $T = 500$ K, (c) $T = 700$ K.

serves as the main factor of amorphization of the Gd_2Fe_{17} composition.

Diffraction peaks of the $GdFe_5$ phase also appear in electronograms (structural type $CaCu_5$), especially distinct at large angles (Fig. 3). The Gd_2Fe_{17} compounds are the closest to the structural type of $GdFe_5$ (φ_1 and φ_2 phases). Pairs of smaller atoms (Fe_2) form these compounds as a result of substitution of 1/3rd larger Gd atoms in the $GdFe_5$ structure.

4. Conclusions

The substrate temperature influences the structure of the examined films significantly. At the substrate temperature of $T_s = 300$ K amorphous films are formed. During heating of such films, the initial crystallization phase consists of a-Fe crystallites. The formation of polycrystalline films with a-Fe and Gd_6Fe_{23} phases completes the process of crystallization of amorphous films of the Gd_2Fe_{17} composition.

Table 1
Decoding the structure of Gd_2Fe_{17} films at $T_s = 500$ K (T_s – substrate temperature)

Gd_2Fe_{17} films at $T_s = 500$ K			Gd_2Fe_{17} in bulk (Structural type Th_2Ni_{17})			Gd_2Fe_{17} in bulk (Structural type Th_2Zn_{17})			$GdFe_5$ in bulk (Structural type $CaCu_5$)		
I/I_0	d_n	*hkl*	I/I_0	d_n	*hkl*	I/I_0	d_n	*hkl*	I/I_0	d_n	*hkl*
70	2.9367	113	30	2.9767	112	82	2.9733	113	40	2.9756	101
55	2.4448	030	43	2.4525	030	73	2.4652	030	26	2.4535	110
100	2.0795	032	46	2.1240	220	26	2.3788	024	35	2.1248	200
45	1.8766	114	100	2.1143	032	100	2.1350	220	100	2.1143	111
40	1.4815	226	28	2.0860	004	97	2.1185	033	30	2.0840	001
55	1.3293	332	22	1.8928	222	53	2.0713	006	22	1.5884	112
30	1.2157	060	35	1.8726	114	32	1.8977	223	21	1.4988	211
25	1.0530	222	17	1.3408	332	24	1.4866	226	30	1.4878	202
25	0.9020	411	15	1.2260	060	27	1.3446	333	34	1.3412	301
						23	1.2326	060	25	1.2268	220
									26	1.2090	113
									37	1.0572	222
									20	0.9919	303
									45	0.9052	411

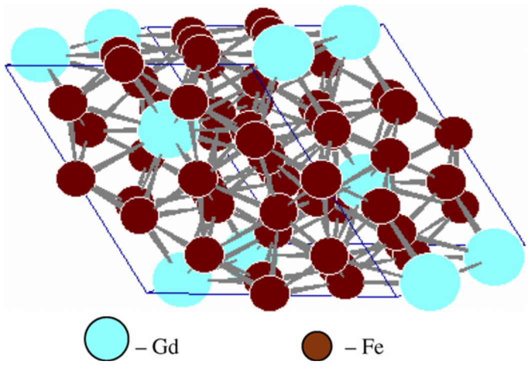

Fig. 3. The structure of Gd_2Fe_{17} of the Th_2Ni_{17} type constructed with the PowderCel computer code l.

The separation of phases in the amorphous state offers the possibility to govern the generation of fine-dispersed a-Fe crystallites in an amorphous matrix.

Upon deposition of films on heated substrates ($T_s = 500$ K), they are transformed into amorphous-crystalline. A different picture can be seen in the kinetics of phase formation under precipitations of Gd_2Fe_{17} films on preheated substrates. At $T_s = 500$ K, the films become amorphous-crystalline. The fraction of polycrystalline phases increases with a further increase in temperature. An analysis of electronograms has shown that the polycrystalline part of films consists of three phases: Gd_2Fe_{17} compounds (60%) of the Th_2Ni_{17} structural type (φ_1 phase), Gd_2Fe_{17} compounds (30%) of the Th_2Zn_{17} structural type (φ_2 phase) and a small amount of $GdFe_5$ compounds (about 10%) of the $CaCu_5$ structural type. The presence of these three phases leads to mutual blocking of crystallites' growth, which determines the possibility of amorphous state formation and high thermal stability.

References

[1] P.I. Krypyakevych, D.P. Frankevych, O.S. Zarechnyuk, High-grade on iron compounds in a 'rareearth metal – iron' systems and their crystalline structures, Visnyk Lvivskogo Universytetu Chemistry 8 (1965) 61.
[2] S.A. Kukushkin, A.V. Osipov, Processes of condensation of thin films, Uspehi Fizicheskih Nauk. 168 (10) (1998) 1083.
[3] V.A. Lagunov, A.B. Sinani, Computer model operation of forming of crystal structure at transition from amorphous state, Fizika Tverdogo Tela. 42 (4) (2000) 1087.
[4] Ye.I. Gladyshevski, O.I. Bodak, Crystal chemistry of intermetallic compounds of rare-earth metals, Vyscha Shkola, Lvov, 1982, p. 250.
[5] P.I. Krypyakevych, D.P. Frankevych, Yu.V. Voroshylov, Compounds with structures such as Th_6Mn_{23} in alloys of rare-earth metals with manganese and iron, Poroshkovaya Metalurgiya 35 (11) (1965) 55.
[6] Yu.A. A.P. Shpak, Yu.A. Kunitskiy, V.L. Karbovskiy, Cluster and nano-structural materials, Akadenperiodika, Kiev, 2001, p. 587.