MAGNETIC PROPERTIES OF THIN FILM ALLOYS OF *f-d* METALS[1]

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The magnetic properties of rare earth metal alloys, namely of Gd—Fe, Gd—Co, Gd—Ni, Sm—Fe, Sm—Co, and Sm—Ni films are studied in dependence of the concentration of the components, structure, phase state and production technology. Domain structure, perpendicular anisotropy, magnetostriction and other magnetic effects are studied and their explanations are proposed.

I. INTRODUCTION

In the past few years rare earth metals (*REM*) and their alloys have been attracting a continually increasing interest of scientists and engineers, as they represent a practically inexhaustible source of materials of unique properties. Large raw material resources of the *REM*, as well as the advance of chemical technology and metallurgy enabling the production of the *REM* of a desired purity (99.9), were helpful to the development of the research into and the application of the *REM* in electronics, aviation, metallurgy, atomic industry, medicine and agriculture.

The use of the *REM* in various fields is based on special properties of their compounds in combination with other chemical elements. Scientists are especially interested in the alloys of the rare earth metals (*f*-metals) with metals of the iron group (*d*-metals) which differ by a large complex of various magnetic properties. It is enough to mention the $SmCo_5$ type compounds having a record value of magnetic energy, or the components of the $TbFe_2$ type with enormous values of magnetostriction.

The magnetic properties of the *REM* and their alloys with Co, Ni, and Fe are described in several fundamental papers which are devoted mainly to the

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study of compact materials while only few papers are known about their thin film properties. However, the investigation of thin films of the *f*- and *d*- metal ccompounds plays an important role in the determination of their specific magnetic properties. Moreover, the contemporary experimental technique allows for the sufficiently effective investigation of thin films. Besides, the thin magnetic films of *f-d* metal alloys may prove to be perspective materials for the construction of universal memory systems with a great capacity. In this way, thin films with perpendicular anisotropy can be used as magneto-optical parts of the short memory and as the magnetic memory on cylindrical domains, as well as long lasting high density records on high coercive films with planar anisotropy.

With respect to the above, it is necessary to find general basic magnetic properties of films of *d-f* metal alloys in dependence on the concentration of components, structure and phase state, as well as on the technology of their production. The present paper, in which the magnetic properties of Gd—Fe, Gd—Co, Sm—Fe, Sm—Co, Gd—Ni and Sm—Ni films are dealt with, is devoted to such topics.

II. TECHNOLOGY AND MAGNETIC PROPERTIES

The films were produced by thermal evaporation of a mixture of components in a vacuum of 10^{-6} mm Hg on organic glass pads and NaCl plates at the temperature of 200 ° with a following annealing at 400—450 °C. The thickness of the condensates was measured by a flint thickness measure and by the use of multiray interference [1]. The chemical homogeneity of films was determined by the microanalyser "Komega MS-46" and the component concentration by means of spectral analysis [2]. Phase state and crystal structure were investigated by the diffractometer "Dron-0.5" and by the electron microscope UEMV-100 K. Magnetization measurements were conducted in a vacuum magnetometer with a perpendicular field [3]. The domain structure was observed by the magneto-optical method and by an electron microscope. The magnetostriction was determined by the interference method [4]. The investigation was performed in a magnetic field of an intensity of up to 24 kOe.

In connection with the big differences in electronegativity and the atomic dimensions of Fe, Co, Ni, and *REM* their mutual solubility is restricted, for example it is 0.2—0.3 weight % for Fe—Gd (at room temperature) [5]. That is the reason why mechanical mixtures and intermetallic compounds are usually produced in *f-d* metal alloy films. The production of compounds is basically related to the phase diagrams for massive samples. As a rule, the produced films are multi-phased and the realization of one-phased states

represents definite technological difficulty. The easiest of all is to produce films where the Laves phase RM_2 is dominant (here *R* stands for the rear earth element and *M* for Co, Ni, Fe). As pointed out in [6], the compounds with the Laves type structure are produced in a film form in gadolinium with intermediate *d*-metals of the interval from manganese to copper. The activity of the phase production is increased by the order number increase of the *d*-element. While a $GdMn_2$ compound is being formed during four hours or more at the temperature of 450 °C, then in the case of $GdNi_2$ the time is shortened to 1.5 hours and the compound $GdCu_2$ is formed instantly after the condensation and subsequent cooling to room temperature. At the same time, in case of condensation on glass plates, the lattice parameters of compounds in a film form are larger than in massive ones, which is explained by the difference in the thermal dilatation coefficients of the film and the plates.

The production of other intermetallic compounds in the form of a film needs an especially elaborated technology. For example, an RM_5 compound can be produced by the evaporation of a mixture of components at a certain speed or by the evaporation of massive RM_5 alloys by the "explosion" method [7].

The differences between the atomic radii of *f* and the *d* metals cause the formation of amorphous films of their alloys [8, 9]. Films of Gd—Fe [10], Gd—Ni [11], Sm—Ni [12] and Gd—Co [13] have at the condensation temperature 200 °C a soft dispersion crystalline structure similar to the amorphous state. The temperature dependence investigation of the electroresistance of $TbCo_5$ films shows that, at the condensation temperature 210 °C, amorphous films are produced with germs of the crystalline phase with a structural stability in a wide range of temperature. The mentioned films preserve the soft crystalline structure after annealing at 400—450 °C. The stage of dispersion of the films may be influenced significantly by means of the variation of the condensation temperature.

The *X*-ray spectral analysis of the above structures has shown their chemical structure homogeneity and the stability of phase composition. It is possible to assume that the stability of the phase state is caused by a thin layer of oxide, covering the surface and preventing thus a further interaction with oxygen.

One of the most important parameters in all cases of the practical application of films is the magnetization *I*. The dependence of *I* on the structure of Gd—Fe Gd—Ni, Sm—Ni and Gd—Co films is shown in Fig. 1. As one can see, a slight change of the component concentration causes a big change in magnetization. The decrease of *I* with an increase of the *REM* components is determined (in case of Gd) by the antiparallel orientation of magnetic moments of *f* and *d* metals and a change of magnetic moments of *d*-metal atoms in consequence of their interaction with *REM* atoms [15]. The difference in the Gd—Ni and

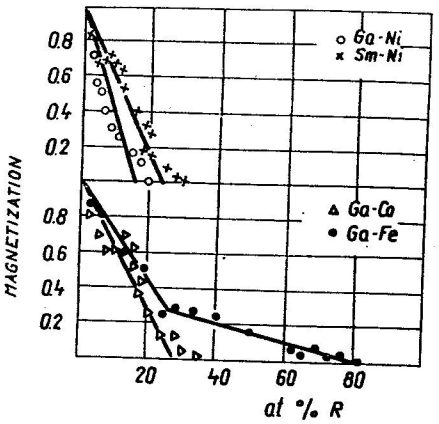


Fig. 1. Magnetization of *f-d* metal alloys as a function of their *REM* contents (h = = 1000 Å, glass pads).

Sm—Ni films magnetization is explained by a different magnetic ordering in these systems. The exceptional change of I in Gd—Fe is related to the fact that in iron the average number of localised 3*d* electrons per one lattice point is equal 6.0, while in Ni and Co it is 9.7 and 8.4, respectively [16]. Therefore, in case of Co and Ni there appears the effect of a filling up of the 3*d* band by conductivity electrons of *REM*. This effect is stronger according to the degree of dilution of the 3*d* metal by gadolinium and causes a weakening of the *d-d* exchange interaction [17].

The change of magnetization as a function of the composition is a specific feature of thin film condensates. Specific properties of *f-d* metal alloys favour possibilities of production of films with perpendicular anisotropy (*PA*) which can be caused by: a) crystalline anisotropy; b) inner isotropic tensions; c) columnar structure of condensates; d) ordering of atomic pairs. Mn—Bi films serve as an example of PA caused by crystalline anisotropy. Thin films of *f-d* metals produced by a gradual sedimentation with a following annealing may have, due to a directed diffusion, a texture with a weak magnetization axis perpendicular to their surface [18]. At high values of magnetostriction of *f-d* metal films the inner isotropic tensions may cause perpendicular anisotropy [19] but, generally, in these cases *PA* is sensitive to thermal procedures and by annealing it gradually disappears completely.

As follows from [9] the pair ordering in amorphous *f-d* films also causes perpendicular anisotropy which in turn causes formation of cylindric magnetic domains (C. M. D.).

The study of Gd—Fe films in a wide range of concentrations has revealed the possibility of producing a labyrint type of domain structure in condensates with a thickness of 800—1000 Å. Fig. 2 presents a picture of the domain structures of $GfFe_2$ and $GdFe_5$ films demagnetized by alternating field of frequency of 50 Hz perpendicular to their surface. The $GdFe_2$ film is characterized by the coercive force $H_c = 50$ Oe and by the field of transition to one domain state $H_p = 80$ Oe. For $GdFe_5$, $H_c = 360$ Oe and $H_p = 410$ Oe. For intermediate structures of Gd—Fe a gradual change of domain structure, H_c and H_p are observed.

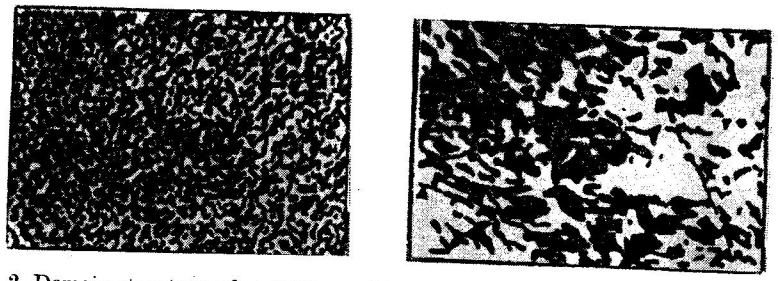


Fig. 2. Domain structure of a) $GdFe_2$ and b) $GdFe_5$ films (h = 1000 Å, glass pads).

In Gd—Co and Gd—Ni film surfaces a single axis magnetic anisotropy is produced [13, 20]. If the condensation temperature is increased, the anisotropy dispersion quickly grows and the film becomes magnetically isotropic.

The investigation of the domain structure of Gd—Co films (~ 34 weight % Gd) produced on NaCl plates at various condensation temperatures has shown that the change into the isotropic state is accompanied by an increase of H_c and by softening of the domain structure up to its disappearance at $T_K \sim 400$ °C (Fig. 3). An analogical change of anisotropy, H_c and domain structure is observed at the annealing of films at the temperature of 500 °C and more. These changes are determined by a decrease of the dispersion level of films at an increasing temperature of condensation and annealing and by

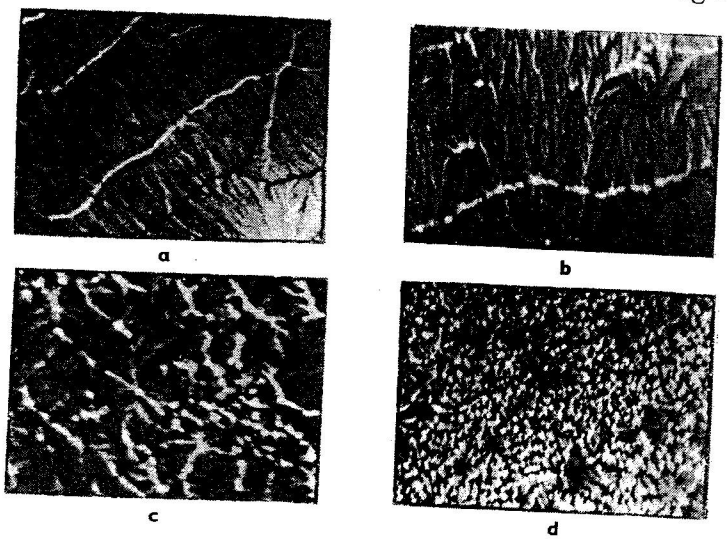


Fig. 3. Domain structure of a Gd—Co film (~ 34 weight % of Gd) produced on an NaCl plate at various condensation temperatures (h = 600 Å). a) $T_K = 280$ °C, $H_c = 60$ Oe; b) $T_K = 310$ °C, $H_c = 90$ Oe; c) 340 °C, $H_c = 140$ Oe; d) $T_K = 370$ °C, $H_c = 220$ Oe.

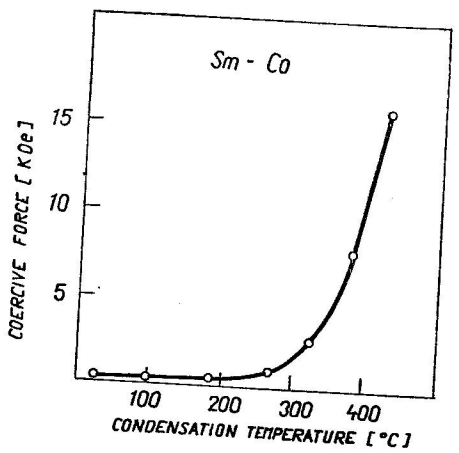


Fig. 4. The coercive force of Sm—Co films (~ 34 weight % of Sm) as function of their production base plate temperature (h = 4000 Å, glass pads).

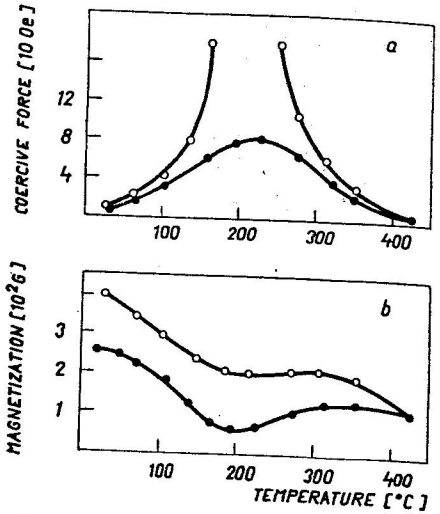


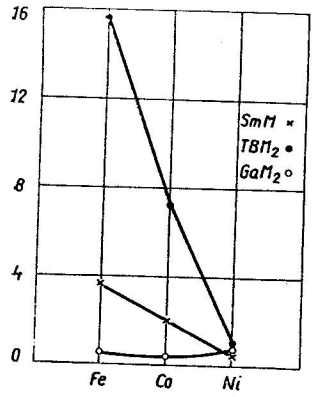
Fig. 5. Thermal change of a) coercive force; b) magnetization; of a film with 30 at. % of Gd, 70 at. % of Fe in the region of the magnetic compensation point (h = 1500 Å).

an increase of crystallographic anisotropy. A definite role is also played by a thickening of the intercrystalline layer which reduces the interaction of atoms in neighbouring film grains.

The investigation of the coercive force dependence on the composition of *f-d* films is very difficult because H_c is a structure sensitive parameter [21] and a slight change in the film preparation technology causes abrupt changes of the force. Therefore, the study of interference of technological parameters on the coercive force is of great interest.

The dependence of H_c on the temperature of the support plate in the Sm—Co film production of a thickness of ~4000 Å is shown in Fig. 4. Films were obtained on glass pads with a temperature gradient from a $SmCo_5$ alloy by the "explosive" method [7]. The change of H_c is explained by an increase of the importance of crystalline anisotropy with an increase of condensation temperature, causing thus the enlargement of the film grains.

When T_k is reduced, the produced *f-d* films are more dispersed, with regions of a coherent scattering of 25 Å and less. The observed values of the coercive force are comparatively not greater for Sm—Co and Gd—Co films either. Small values of H_c could be explained by the fact that the width of the domain boundaries is grater than the coherent scattering region and that the movement of walls is not hindered by energetical barriers connected with the periodicity of the substructure.



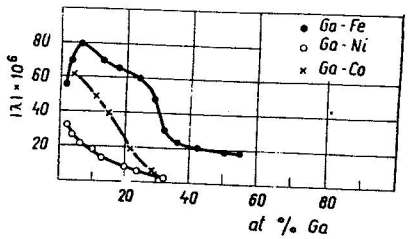


Fig. 7. Magnetostriction of a RM_2 compound film as a function of the *d*-component.

Fig. 6. Magnetostriction of *f-d* metal alloys as a function of the Gd content (h = 800—1000 Å, organic base plates).

Let us investigate the change of H_c in the region of the magnetic compensation temperature Θ_k. As it is known, the point of the magnetic compensation is not the phase transition point with a change of magnetic properties characterized by the Curie and Neel points. Moreover, in the Θ_k region H_c undergoes anomalous changes. The change of H_c of a film composed of 30 at. % Gd and 70 at. % Fe in the region Θ_k is shown in Fig. 5a. Corresponding changes of magnetization are shown in Fig. 5b [19]. H_c reaches the maximum value at the point of magnetic compensation. In polycrystalline films, because of structural imperfection, the full compensation is often not reached and the sharp maximum of H_c is not observed.

A typical feature of *REM* is the huge magnetostriction λ [22]. The higher value of elastic magnetic effects is qualitatively explained by a strong orbital interaction in these metals caused by the localization of electrons.

High values of λ may be caused either by electrostatic interaction of an anisotropic cloud of 4*f* electrons with the crystal field of the lattice [23], or by the anisotropy of indirect exchange interaction through conductivity electrons [24].

The *REM* component of *f-d* metal alloys influences substantially their magnetoelastic properties. Yet, for the alloy films of gadolinium with Co, Ni, Fe no higher values of magnetostriction are characteristic (Fig. 6) [13, 25]. This is related to the fact that Gd ions are in the *s*-states, i. e. they do not have an orbital momentum and they cannot contribute very much to the λ of *f-d* metal compounds.

The increase of magnetostriction of Gd—Fe films in the range of a gadolinium concentration of up to 6 at. % is caused by an increase of the Gd_2Fe_{17} phase. A further increase of the content of the *REM* component causes the decrease of λ in connection with the phase state change and the change of magnetization

(Fig. 1). The dependence of magnetostriction of Gd—Co and Gd—Ni films on the content of the *f*-metal is determined by the change of magnetization. Magnetostriction of SmM_2, TbM_2, GdM_2 at 120 °C is shown in Fig. 7. As we have mentioned earlier, the lowest values of λ are observed in case of Gd. At the same time, with the increase of the order number of the *d*-metal, the decrease of magnetostriction is observed. This is explained by a decrease of the *f-d* exchange interaction. The highest values of λ are observed for compounds with terbium.

III. CONCLUSION

In conclusion one can say that the change of dilution of *d*-metal by ***REM*** causes a remarkable change of magnetic properties of films at normal temperature. The phase state and the substructure together with the components concentration show a great influence on the anisotropy, domain structure and coercive force of films.

The variety of magnetic properties of *f-d* alloy films offers many possibilities for their practical use in all sorts of devices with magnetic recording in computers.

Yet, in order to solve practical problems, deep knowledge of the interrelation of the structure, composition and magnetic properties of *f-d* metal films will be required. Therefore a special attention has to be paid to the technological development of the single phase polycrystalline sample production, to the production and investigation of amorphous films and to the study of the nature of high coercive states of $SmCo_5$ and $GdCo_5$ films.

REFERENCES

[1] Durasova Yu. A., Nikitina T. A., Izvestiya AN SSSR, *29* (1965), 657.
[2] Karabanová B. P., *Sb. Apparature i metody issledovaniya tonkich magnitnych plenok*, Krasnoyarsk, 1968.
[3] Shelkovnikov V. N., *Sb. Apparature i metody issledovaniya tonkich magnitnych plenok*, Krasnoyarsk, 1968.
[4] Yakovleva K. A., Buravichin V. A., Doklady AN SSSR *175* (1967), 66.
[5] Savickij E. M., Terechova B. F., Burov I. B., Szistyakov O. D., JICH *7* (1961), 1732.
[6] Domyshev B. A., Egorov B. A., Buravichin V. A., Sidorenko L. M., Luzgin N. I., FMM *28* (1974), 102.
[7] Young A. S., Heretage R. J., Vacuum *18* (1968), 147.
[8] Mader S., J. Vac. sei. Techn. *2* (1965), 35.
[9] Chaudhari P., Cuomo J. J., Gambino R. J., *IBM, J. Res. Develor* New York 1973, 10598.
[10] Buravichin V. A., Inyutin A. I., Nedelko A. A., Kleschinskij L. I., Egorov V. A., *Sb. Fizika magnitnych plenok 2*. Irkutsk 1970.

[11] Buravichin V. A., Boczkarev V. F., Egorov V. A., Budanov O. P., *Sb. Fizika magnitnych plenok 4*, Irkutsk 1971.
[12] Buravichin V. A., Shelkovnikov V. N., Kameneva G. A., Egorov V. A., Manakov N. A., *Sb. Fizika magnitnych plenok 5*, Czita 1972.
[13] Aschepkov V. T., Ayushjav G., Buravichin V. A., Damba L., Domyshev V. A., Luzgin N. I., *Trudy instituta fiziki i matematiki AN MNR*, 12 Ulan-Bator 1973.
[14] Egorov V. A., Martynova T. M., *Sb. Fizika magnitnych plenok 5*, Czity, 1972.
[15] Belov K. P., Belyanczikova M. A., Levitin R. Z., Nikitin S. A., *Redkozemelnye ferro- i antiferromagnetiki*. Izd. Nauka, Moskva 1965.
[16] Batterman B. W., Chipman D. R., de Marco J. J., Phys. Rev. *112* (1961), 68.
[17] Lemaire R., Passard D., Pauthens R., Schweizer J., J. Appl. Phys. *39* (1968), 1092.
[18] Stoffel A. M., J. Appl. Phys. *39* (1968), 563.
[19] Buravichin V. A., Nedelko A. A., Shelkovnikov V. N., *Sb. Fizika magnitnych plenok*, Irkutsk 1968.
[20] Shelkovnikov V. N., Kameneva G. A., Manakov N. A., *Sb. Fizika magnitnych plenok 4*, Irkutsk 1971.
[21] Palatnik L. S., Fuks M. Ya., Kosevicz 4. M., *Mechanizm obrazovaniya i substruktura kondensirovannych plenok*. Izd. Nauka, Moskva 1972.
[22] Belov K. P., Levitin R. Z., Ponomarjov B. K., J. Appl. Phys. *39*, (1968), 3285.
[23] Kasuya T., *Magnetism*. Academic Press. Ed. by Rado G. and Suhl H. *2 B* (1966), 216.
[24] Irjin Yu. I., JETF *50* (1966), 379.
[25] Buravichin V. A., Domyshev V. A., Uschapovskij L. V., Kazakov V. G., Aschepkov B. T., *Sb. Fizika magnitnych plenok 3*, Irkutsk 1970.

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