Magnetic properties of amorphous and nanoscrystalline FINEMET type iron-based alloys

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Temperature dependences of magnetic susceptibility for rapidly quenched FINEMET type $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ (Me = Zr, Nb, Mo) amorphous alloys have been studied by Faraday technique within 300 to 900 K temperature range. The values of Curie temperature, magnetic moment per iron atom and crystallization temperature have been determined. These parameters were found to be dependent on difference of the number of *d*-electrons in Fe and Me atoms. The revealed peculiarities in paramagnetic susceptibility behavior are connected directly with the structure evolution processes in the rapidly quenched ribbons. This evolution consists in the size increasing of crystal-like inclusions of silicon solid solution in α-Fe. Magnetically, these inclusions behave as super-paramagnetic particles.

Методом Фарадея исследованы температурные зависимости магнитной восприимчивости быстрозакаленных сплавов типа FINEMET $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ (Me = Zr, Nb, Mo) в интервале температур 300–900 К, определены их температура Кюри, магнитный момент на атом железа и температура кристаллизации. Установлено, что эти параметры коррелируют с разностью *d*-электронов Fe и Me. Обнаруженные особенности в поведении парамагнитной восприимчивости непосредственно связаны с процессами структурной эволюции быстрозакаленных лент, которая заключается в увеличении размеров кристаллоподобных включений твердого раствора кремния в α-Fe. Эти включения в магнитном отношении ведут себя как суперпарамагнитные частицы.

Recently, the rapidly quenched FINEMET type alloys are of a special interest keeping in mind the prospects of their industrial application. Nanocrystalline state is formed easily in these alloys after certain heat treatment. This process is accompanied by corresponding modification of the important service properties. In [1], presented is the way to nanocrystalline state by controlled annealing of $Fe_{73.5}Cu_1Nb_3Si_{13.5}B_9$ amorphous alloy. The report is of a great interest because such alloys were found to be similar in the level of their magnetic characteristics (high magnetic permeability and saturation induction, nearly zero magnetostriction and low magnetization losses) to the precision cobalt-based magnetic alloys (in particular, to amorphous ones). 75–80 % of nanocrystalline α-Fe(Si) phase is formed in $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ rapidly quenched alloys of FINEMET type (where Me is transition metal). These nanocrystallites of 10 to 100 nm size (depending on Me type) are embedded in the residual amorphous matrix [1–3]. The nanocrystallization of such alloys occurs at 480–550°C within the frame of so-called main transformation [4]. Numerous works deal with the studies of FINEMET alloys. To date, the influence of Me type on the nanocrystalline state formation processes has been studied quite comprehensively [5]. The composition and structure of nanocrystals [6] have been studied, too. The role of the residual amorphous phase in the attaining of optimum service characteristics has been explained [7]. The silicon content in nanocrystalline phase was found to be essentially dependent on the temperature-temporal parameters of heat treatment and to vary within 2 to

21 % range [8]. The presence of dopants influences significantly the atomic structure and structure-sensitive characteristics of the FINEMET alloys and parameters of their stability against external actions.

However, some aspects remain still far from understanding in spite of the intense investigations of this class of materials. In particular, only fragmentary and even inconsistent data on thermomagnetic studies of $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ FINEMET alloys depending on Me type are available in literature (the main attention has been paid to the alloys of routine composition with Me = Nb). Besides, the initial stages of nanocrystallization have been studied in detail in [9]. It was shown that the pre-crystallization structure reconfigurations in the alloys occur even at the annealing temperatures of about 350°C. This is confirmed by the increased X-ray small angle scattering, though till now, the nanocrystallization in those alloys was believed to occur at essentially higher temperatures.

So, the aim of this work was to study comprehensively the thermomagnetic characteristics of FINEMET type $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ metal alloys containing different dopants (Me). A special attention was paid to the behavior of their magnetic properties within the temperature range where, according to [9], certain structural transformations already take place.

The 2 mm wide and 30–40 μm thick ribbon-shaped samples of FINEMET type $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ (Me = Zr, Nb, Mo) metal alloys have been prepared by single-roll quenching technique using high purity (better than 99 %) initial materials. The rotation speed of the quenching disk of 600 mm in diameter made of chromic bronze was 820–850 min^{-1}. The ejecting pressure was varied from 15 to 20 kPa. All the as-prepared ribbons were amorphous that has been confirmed by the X-ray diffraction. The composition of the rapidly quenched ribbons was controlled by the X-ray fluorescence analysis. The magnetometric investigations were carried out in the temperature range 300–900 K in the field of 550 kA/m under purified argon medium using Faraday-type magnetometer with microbalance. The accuracy of the susceptibility measurements $\Delta\chi/\chi$ was better than 1 % and of the temperature ones, $\Delta T \leq 0.5$ K. The heating rate was 8 K/min. The samples for magnetic measurements were about 0.5×0.5 mm^2 in size.

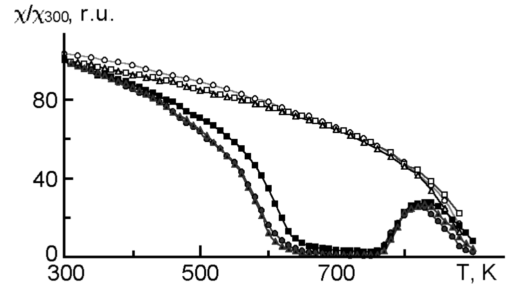

Fig. 1. Thermomagnetic curves for $Fe_{73.5}Cu_1Mo_3Si_{13.5}B_9$ amorphous alloys: Me = Zr (squares), Nb (triangles) and Mo (circles) (solid symbols correspond to heating, open symbols, to cooling).

Fig. 1 presents the temperature dependencees of the normalized magnetic susceptibility χ/χ_{300} for three rapidly quenched $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ alloys (Me = Zr, Nb, Mo). These dependences were obtained for the full heating-cooling cycle within the range of 300–900 K. The general character of thermomagnetic curves is seen to be similar for all studied alloys and proves them to be ferromagnetic at moderate temperatures. The magnetization of the samples reduces rapidly upon heating and, starting from a certain temperature, which is the Curie point of the amorphous state (T_c), a wide paramagnetic region is observed (>150 K). Upon further heating, an essential increase of magnetization is observed due to formation of only one (judging from the cooling branch shape of the experimental curves) ferromagnetic phase with a significantly higher Curie temperature. According to the data from [6, 9] as well as to the results of our X-ray diffraction experiments, this phase is a solid solution of silicon in α-Fe. The Curie temperature values for the as-prepared samples and after heating to 900 K have been determined from $\chi(T)$ curves using a routine procedure [10]. The values obtained are presented in Table 1. In the case of Me = Nb, those are seen to be in a good agreement with the data reported in [11]. The silicon content in the formed nanocrystalline α-Fe(Si) phase is 19–20 %, as it follows from the found Curie temperatures and data from [12]. This is in a fairly good coincidence with the data from [9] obtained under similar heat treatment conditions. Table 1 contains also the crystallization onset temperatures T_x for the studied alloys. As is seen from Table 1, the parameters indicated exhibit a distinct trend to reduction in the Zr → Nb → Mo se-

Table 1. Curie temperatures and crystallization start temperatures of rapidly quenched $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ ribbons

Me	T_c, K		T_x, K
	Amorphous ribbon	Crystallized ribbon	
Zr	637	915	760
Nb	614	900	760
Mo	608	890	742

quence, i.e. at the reducing difference between the numbers of Fe and Me d-electrons. This could indicate an important role of the electron factor in defining the thermal stability parameters of the studied alloys.

The broad paramagnetic region made it possible to study the temperature dependences of specific paramagnetic susceptibility $\chi(T)$ for the samples. Fig. 2 presents the obtained $\chi(T)$ dependences. Magnetic susceptibility for all the studied alloys drops rapidly with temperature. Judging from the experimental data, these dependences in $T_c < T < T_x$ temperature range could be fitted by the equation:

$$\chi = \chi_0 + \frac{N\mu^2}{3k(T - \theta)}. \quad (1)$$

Here, χ_0 is a temperature-independent term in susceptibility; μ, the effective paramagnetic moment per atom of alloy; θ, the paramagnetic Curie temperature; k and N, the Boltzmann constant and the Avogadro number, respectively. The first term in Eq.(1) includes paramagnetic contribution due to conduction electrons and ion core diamagnetism. The second (Curie-Weiss like) term in Eq.(1) which is due to magnetism of the magnetic moments localized on atoms has been found to be dominant for all the studied alloys. This is evidenced also by the character of $\chi(T)$ curves.

At the same time, it is seen in Fig. 3 that the character of susceptibility variation is in fact more complex than in the case of an ensemble of weakly interacting magnetic moments, since the temperature dependence of reciprocal magnetic susceptibility is somewhat nonlinear. $\chi^{-1}(T)$ curves could be fitted well by two lines with different slopes (such behavior is the most pronounced in a case of ribbons containing Zr and Nb). It should be noted that the temperature corresponding to the knee in $\chi^{-1}(T)$ dependences, almost coincides with the temperature at which, according to [9], the structural reconsruction processes start in the studied ribbons. These processes are characterized both by a noticeable size increase of crystal-like nuclei (up to 2.8 nm) and increasing volume fraction thereof.

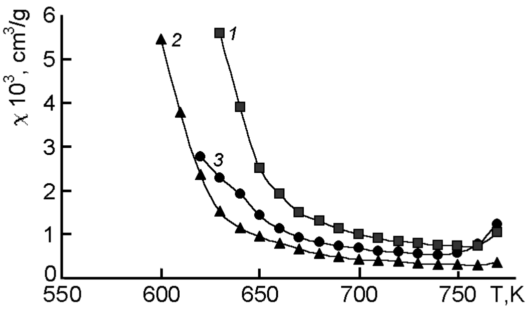

Fig. 2. Temperature dependences of paramagnetic susceptibility for $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ amorphous alloys (Me = Zr(*1*), Nb(2) and Mo(3)).

The magnetic characteristics of the samples obtained from Eq.(1) (localized magnetic moment per Fe atom μ_{Fe} and paramagnetic Curie temperature θ) are listed in Table 2. The μ_{Fe} values were calculated using the following equation:

$$\mu_{Fe} = \frac{\mu}{c^{1/2}},$$

where $c = 0.735$ is the atomic fraction of iron in the studied alloys. It is known that for pure iron, the localized magnetic moment can be calculated from the formula:

$$\mu_{Fe} = \sqrt{4S(S+1)}, \quad (2)$$

where $S = 3/2$ is the spin of Fe atom [13]. The calculated value of $\mu_{Fe} = 3.87\mu_B$ (Eq.(2) is essentially lower as compared to the experimental data for the studied as-prepared alloys (and all the more for nanocrystalline samples). This points to the presence of structure inhomogeneities even in the initial amorphous material. These inhomo-

Table 2. Magnetic characteristics of amorphous and nanocrystalline $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ alloys

Me	μ_{Fe}, μ_B		θ, K	
	Amorphous	Nanocryst.	Amorphous	Nanocryst.
Zr	6.56	8.30	618	568
Nb	4.81	–	602	–
Mo	5.56	7.52	609	513

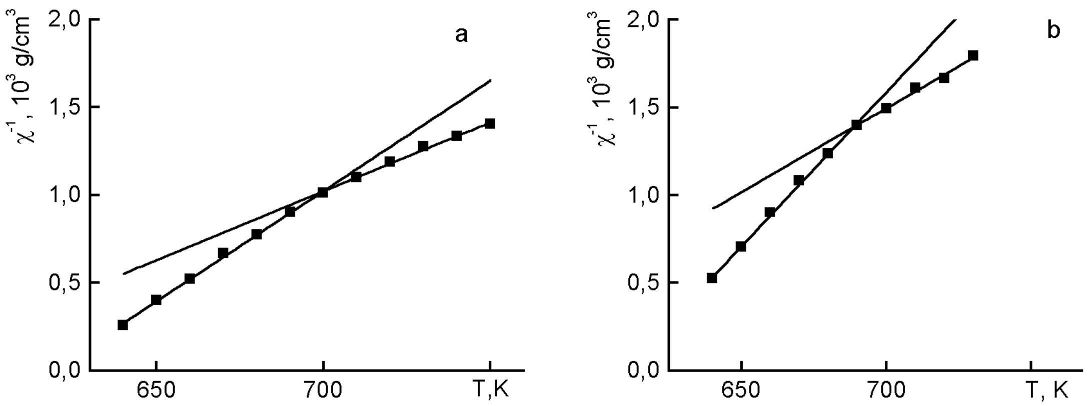

Fig. 3. Temperature dependences of reciprocal magnetic susceptibility for $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ (Me = Zr (a) and Nb (b)) amorphous alloys.

geneities (or so-called "quenched centers") are iron-enriched clusters with parallel orientation of the atomic magnetic moments. The estimated size of such clusters agrees well with the results of the X-ray small angle scattering [9].

Numerous experimental studies of amorphous materials (see, for example, [9, 14]) allow to state that the atomic structure characteristics of the rapidly quenched alloys and, consequently, the level of structure-sensitive parameters (in particular, the values of magnetic moment) depend essentially both on quenching conditions and on the alloy composition. It is just these circumstances that, in our opinion, could define the revealed dependence of the Fe atom magnetic moment on the Me type. In fact, it is well known that the iron possesses a number of allotropic modifications (α-, γ- and δ-Fe) with different types of the atomic nearest neighboring. During quenching, the melt passes step by step the temperature intervals of stability for those modifications. Hence, the local atomic symmetry within various areas of the ribbon could inherit the character of any Fe modification, depending on the alloy composition as well as on quenching conditions (cooling rate, the melt overheating temperature, etc.), which are somewhat different for the alloys containing different Me types.

As it was stated above, $\chi^{-1}(T)$ dependences for the studied alloys are of a nonlinear character and could be approximated by two straight lines with different slopes. The knee in $\chi^{-1}(T)$ curves presented in Fig. 3 is observed at 700 and 689 K, for Me = Zr and Me = Mo, respectively. The stated peculiarity, to our mind, is defined directly by the atomic structure evolution in the rapidly quenched alloys. It proceeds rather intensely in this temperature range and consists in a noticeable increasing of the nanocrystalline phase grain size. This phase is the grains of α-Fe based solid solution of silicon [9]. These inclusions are characterized by the parallel orientation of spins for Fe atoms. Judging from the character of the component redistribution at nanocrystallization of FINEMET type amorphous alloys [3, 6, 15], the residual amorphous matrix becomes enriched in nonmagnetic components (Me, Cu) which are predominantly concentrated at the nanocrystal/amorphous phase boundaries. This results in an essential weakening of the exchange interaction between nanocrystalline inclusions and amorphous matrix. As a result, the paramagnetic Curie temperature has to decrease. It is just such a behavior we have observed in experiment. This is distinctly displayed by the data listed in Table 2. Taking into account the above, the α-Fe(Si) nanocrystals formed at initial stages of the structural evolution could be considered as super-paramagnetic particles. The alloys become ferromagnetic only at elevated temperatures (higher than T_x), when the nanocrystals reach sizes exceeding 10 nm [9].

So, the magnetic characteristics of the FINEMET type $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ alloys were found to be sensitive to changes in the atomic structure of the ribbons even at initial stages of the structure evolution at temperatures essentially lower than the crystallization temperature. Thus, the magnitometric measurements could be considered as an effective method to control the structural state of the rapidly quenched ribbons.

To conclude, the temperature dependences of magnetic susceptibility for the

FINEMET type $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ (Me = Zr, Nb, Mo) amorphous alloys have been studied by the Faraday technique. The Curie and crystallization temperatures show a distinct trend to decrease at decreasing difference between the number of d-electrons in Fe and Me atoms. This could point to an important role of the electron factor in defining the stability parameters of the studied amorphous alloys. The value of localized magnetic moment per iron atom was found to be essentially higher that calculated basing on the number of unpaired electrons inherent in pure iron. This could be an evidence to the presence of structural inhomogeneities (i.e., clusters of ferromagnetic type) in the as-prepared amorphous material. The nonlinear character of $\chi^{-1}(T)$ curves is directly conditioned by the evolution of ribbon atomic structure at heating. The revealed evolution consists in increasing size of the crystal-like inclusions of α-Fe based solid solution of silicon. These inclusions could be considered as super-paramagnetic particles because the exchange interaction between them is essentially weakened due to the element redistribution occurring at nanocrystallization of the studied amorphous alloys.

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Магнітні властивості аморфних та нанокристалічних сплавів типу FINEMET на основі заліза

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Методом Фарадея досліджено температурні залежності магнітної сприйнятливості швидкозагартованих аморфних сплавів типу FINEMET $Fe_{73.5}Cu_1Me_3Si_{13.5}B_9$ (Me = Zr, Nb, Mo) в інтервалі температур 300–900 К, визначені їх температура Кюрі, магнітний момент на атом заліза та температура кристалізації. Встановлено, що ці параметри корелюють з різницею d-електронів Fe та Me. Виявлені особливості у поведінці парамагнітної сприйнятливості безпосередньо пов'язані з процесами структурної еволюції швидкозагартованих стрічок, що полягає у збільшенні розмірів кристалоподібних включень твердого розчину кремнію в α-Fe. Ці включення у магнітному відношенні поводять себе як суперпарамагнітні частинки.