COMPARISON OF THE INFLUENCE OF Al ADDITION ON THE MAGNETIC PROPERTIES OF FINEMET AND NANOPERM TYPE ALLOYS

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SUMMARY

We have investigated the influence of aluminium substitution for iron on the magnetic properties of amorphous and nanocrystalline $Fe_{73.5-x}Al_xNb_3Cu_1Si_{13.5}B_9$ alloys (x = 0, 1, 2, 3, 5 and 7 at. %) and $Fe_{88-x}Al_xZr_7B_5$ alloys (x = 0, 1, 3, 5, 7 and 9 at. %). The low-temperature thermomagnetic curves are found to obey the Bloch's $T^{3/2}$ law, for both series of samples. Aluminium in the amorphous FeZrB alloys enhances the value of magnetization. This enhancement is especially pronounced at room temperature. The spin-wave stiffness constant and the Curie temperature also increases with aluminium content. Such an increase was observed only for low concentration of aluminium (up to 2-3 at. %) in the amorphous FeNbCuSiB samples. The analysis of the relationship between the spin-wave stiffness constant and the Curie temperature indicate that in FeNbCuSiB alloys the direct exchange interaction is confined to the nearest neighbours only, while in FeZrB alloys there is a superexchange between the next-nearest neighbour magnetic atoms. This is one of the reasons, why the noncollinear spin structure exists in FeZrB type metal glasses. The increase of magnetization, Curie temperature and spin-wave stiffness can be understood as a consequence of facilitating the long-range order of spins and suppression of spin frustrations by aluminium.

Keywords: *amorphous, nanocrystalline, magnetic properties, spin-waves*

1. INTRODUCTION

The nanocrystalline FeNbCuSiB (Finemet) and FeZrB (Nanoperm) type alloys, prepared by primary crystallization of melt-spun amorphous precursors, are known as materials with excellent soft magnetic properties [1,2]. It was found that small addition of some alloying elements in these alloys may have significant influence on their magnetic properties. Aluminium as alloying element has attracted the attention of the investigators particularly, due to the fact that when replacing iron in small concentration, it can improve the coercivity, saturation magnetization and other magnetic properties of the FeNbCuSiB and FeZrB alloys [3-6]. Up to now mostly small additions of Al (up to 3 at. %) into the aforementioned alloys have been investigated [7,8].

In this work we study the influence of aluminium substitution for iron on the magnetic properties in a wider concentration range, in the $Fe_{73.5-x}Al_xNb_3Cu_1Si_{13.5}B_9$ alloys up to 7 at. % of Al and in the $Fe_{88-x}Zr_7B_5Al_x$ alloys up to 9 at. % of Al. We also try to compare this influence in the two investigated sample series.

2. EXPERIMENTAL PROCEDURE

Ribbon-shaped specimens of $Fe_{73.5-x}Al_xNb_3Cu_1Si_{13.5}B_9$ with x=0,1,2,3,5,7 (marked as FeAlNbCuSiB) and $Fe_{88-x}Al_xZr_7B_5$ with x = 0,1,3,5,7,9 (marked as FeAlZrB) alloys were prepared from the molten master alloys by the rapid quenching method. The specimens were 20 – 30 μm thick and 2 – 3 mm wide.

The FeAlZrB samples were submitted to isothermal heat treatment at temperatures corresponding to their crystallization temperature obtained from the temperature dependence of magnetization for each sample (see Tab. 1). The heat treatments of FeAlNbCuSiB samples were performed at temperatures 763 K and 823 K (490 °C and 550 °C). All samples were annealed for 1 hour in a vacuum furnace.

Temperature dependence of magnetization was measured by vibrating sample magnetometer from 4,2 K to room temperature and further to 1100 K in external magnetic field of 1T and 0,2 T respectively, at the constant heating rate of 10 K/min. The external magnetic field was applied in the plane of the sample. The anisotropy and demagnetizing fields were neglected in the calculations.

3. RESULTS AND DISCUSSION

3.1 Thermomagnetic measurements

Monotonic decrease in magnetization with temperature is observed in the temperature range from 4.2 K to the Curie temperature of the amorphous phase T_{Cam}. There are no magnetic transitions between T_{Cam} and the crystallization temperature T_{cr}. At the crystallization temperature the magnetization increases rapidly due to the major precipitation of ferromagnetic bcc Fe-Si(Al) for FeAlNbCuSiB (or Fe for FeAlZrB) nanograins from

the amorphous matrix. Around 860 K (depending on the Al concentration) the magnetization starts to decrease again, until the temperature reaches the Curie temperature of the crystalline phase. The Curie temperatures T_{Cam}, and the crystallization temperatures T_{cr} are summarized in Tab. 1.

Tab. 1 Curie temperatures of the amorphous phase (T_{Cam}) and crystallization temperatures (T_{cr}) for the FeAlNbCuSiB and FeAlZrB samples.

	FeAlNbCuSiB		FeAlZrB	
x (at%)	T_{Cam} (K)	T_{cr} (K)	T_{Cam} (K)	T_{cr} (K)
0	601	786	327	777
1	606	783	328	785
2	618	781		
3	611	788	350	789
5	585		374	793
7	530		387	803
9			394	819

3.2 Low-temperature magnetization

A number of papers have reported [9] that the amorphous ferromagnets as well as the crystalline ones, exhibit well defined spin-wave excitations at low temperature, which satisfy the normal ferromagnetic energy dispersion relation:

$$E_q = \Delta + D(T)q^2 \qquad (1)$$

where $D(T)$ is the spin-wave stiffness constant, q is the magnitude of the magnon wave-vector and Δ is the effective energy gap.

The temperature dependence of the saturation magnetization in the temperature range of $0<T<T_C/3$ can be then described by the Bloch relation [10]:

$$\frac{M(T)}{M(0)} = 1 - F(3/2, t_h)\, bT^{3/2} - F(5/2, t_h)\, cT^{5/2} \qquad (2)$$

The function $F(s,t_h)$ is the Bose-Einstein integral function and t_h is the gap temperature. The parameter b and c in (2) is related to the spin wave stiffness constant D (if neglecting its temperature dependence) and mean range of exchange interactions $\langle r^2 \rangle$ through the relations:

$$b = 2.612\, \frac{g\mu_B}{M(0)} \left(\frac{k_B}{4\pi D} \right)^{3/2} \qquad (3)$$

$$c = 1.341\, \frac{3\pi\, g\mu_B}{4M(0)} \left(\frac{k_B}{4\pi D} \right)^{5/2} \langle r^2 \rangle \qquad (4)$$

where k_B is the Boltzmann constant, g is the gyromagnetic factor (≅ 2.1), μ_B is Bohr magneton and H is the effective magnetic field.

We have fitted the low-temperature part of the experimental thermomagnetic dependences (below $2/3T_C$) by the least square method. The dependences were found to obey the Bloch's $T^{3/2}$ law for both series of samples, thus the spin-wave stiffness constant was calculated. From the extrapolated values of saturation magnetization $M_s(0)$ we have calculated the average magnetic moment per magnetic atom. In the case of FeAlNbCuSiB samples only the Fe atoms, while for FeAlZrB samples both the Fe and Zr atoms were considered to be magnetic (marked as $\mu_{Fe}(0)$ and $\mu_{Fe+Zr}(0)$), referring to some authors, who found that in FeZr type alloys the Zr atom bares a small negative magnetic moment (-0.4 μ_B) [11].

As-quenched samples: Fig. 1 illustrates the correspondence between the calculated spin-wave stiffness constant and the Curie temperature, which

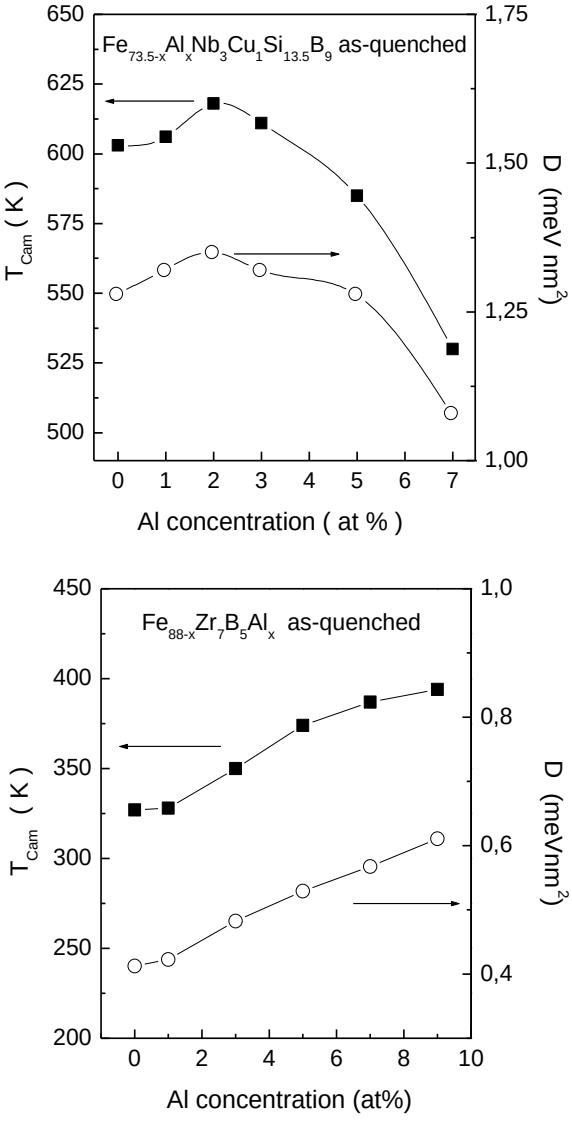

Fig. 1 Concentration dependence of the spin-wave stiffness constant and the Curie temperature of the investigated as-quenched alloys.

seems to be hold in both sample series over the whole concentration range.

The Heisenberg model predicts for a cubic ferromagnet the following linear relationship between D and T_C [12]:

$$D = D_0 + mT_C \qquad (5)$$

with $\quad m = k_B a_1^2 / 2(S+1)$

$$D_0 = z_2 J_2 \left(a_2^2 - a_1^2\right) S/3$$

where S is the localized atomic spin, z_2 is the next-nearest magnetic coordination number, J_2 is the exchange constant between the next-nearest neighbours and a_1 and a_2 are the nearest neighbour and next-nearest neighbour distances, respectively.

Generally, the linear relationship between D and T_C, ($D = mT_C$) passing through the origin is expected for ferromagnetic materials. However, in many amorphous alloys the dependence $D = D_0 + mT_C$ with negative as well as positive D_0 was observed. A positive value of D_0 is obtained if the direct Heisenberg interaction is assumed to be extended to the next-nearest spins. Calculations [13] taking into account the RKKY interaction give a small negative value for D_0 .

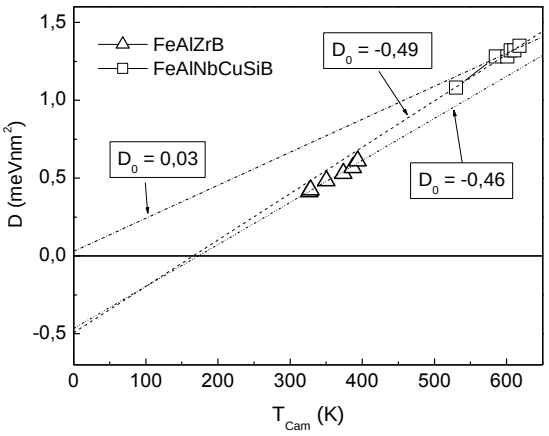

Fig. 2 Relationship between the spin-wave stiffness constant and the Curie temperature in the investigated as-quenched samples.

Fig.2 shows the relationship between the spin-wave stiffness constant D and the Curie temperature T_{Cam} for the investigated as-quenched samples. The dependence is nearly linear in the whole investigated range. Our experimental results follow a relation $D = D_0 + mT_C$ with D_0 = -0.46 ± 0.1 meVnm^2 for FeAlZrB samples. This value is not small and indicates, that in these types of alloys the superexchange interactions mediated by the metalloid and Zr atoms can play important role. These interactions are expected to lead to an antiferromagnetic coupling between the moments of the next-nearest neighbour transition-metal atoms as it is considered in [12]. Their strength can be comparable in magnitude to that of the direct Heisenberg exchange between the nearest neighbours. The superexchange interactions with antiferromagnetic exchange can be one of the reasons of the asperomagnetic spin structure in these type of materials [14,20]. The asperomagnetic structure means that the magnetic moments are canted (as a result of spin frustration in the zones with high nearest neighbour distance mismatch) but they have some long-range preferred orientation in direction – the magnetic structure is not ideally collinear and the magnetic moment of Fe calculated from the saturation magnetization in these alloys is smaller than in pure iron. The strong dependence of the magnetic moment on the Al content in FeAlZrB alloys (Fig. 3) may indicate the existence of the asperomagnetic spin structure.

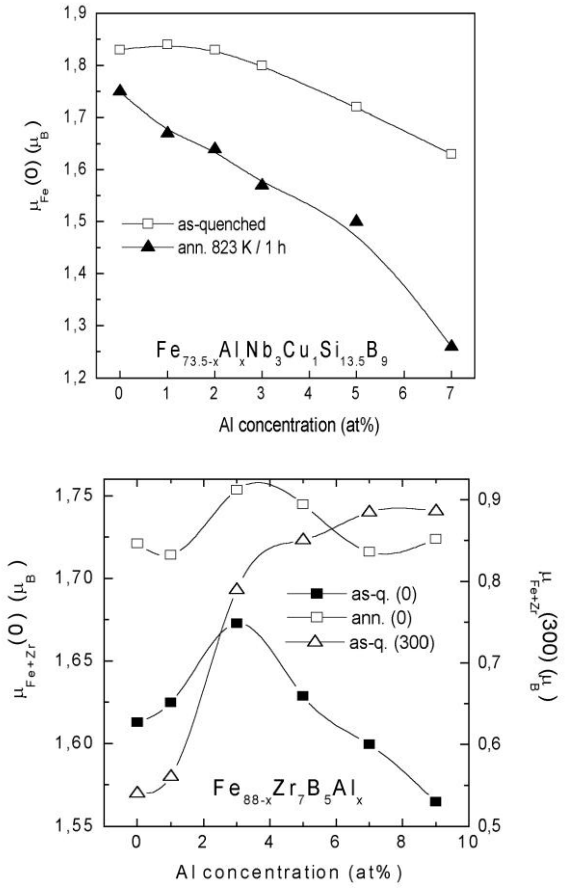

Fig. 3 Concentration dependence of the magnetic moment per magnetic atom in the investigated alloys in as-quenched state and after annealing.
((0): extrapolated to 0 K, (300): measured at room temperature).

The concentration dependence of the magnetic moment $m_{Fe+Zr}(0)$ of as-quenched FeAlZrB samples exhibits a relatively sharp maximum at the concentration of Al about 3 at. %. This maximum

(even though much flatter) is visible also in the case of annealed samples. We suppose that the addition of a few at. % of Al in these alloys suppresses the frustrations and promotes the long-range orientation of Fe spins, thus the magnetic moment does not decrease as a consequence of the dilution effect, but it even increases (up to 3 at. % of Al). Al probably suppresses the local magnetocrystalline anisotropy as it is considered in [15,5]. At higher concentration (above 3 at. % of Al) the dilution effect prevails and the magnetic moment in as-quenched samples decreases in accordance with the decreasing Fe content in the alloy. The depressing effect of Al on the local anisotropy is more apparent in as-quenched FeAlZrB samples at room temperature. The magnetic moment $m_{Fe+Zr}(300)$ (Fig. 3) strongly increases between 1 and 4 at. % of Al with a tendency to saturate above 7 at. %. The additional thermal energy reduces the local anisotropy barriers and enables to emphasise the role of Al.

The concentration dependence of the magnetic moment in the as-quenched FeAlNbCuSiB samples is not as strong as in the FeAlZrB ones. Only a very slight increase up to 2 at. % of Al is observed (Fig. 3). The disturbance of the collinear magnetic arrangement is probably much weaker in these alloys, thus the influence of the Al in this case is not so distinct. Despite, the linear fit of the relation $D = D_0 + mT_C$ gives a value of D_0 = -0.49 ± 0.2 meVnm^2. On the basis of the above discussion much lower D_0 values for the FeAlNbCuSiB alloys are expected. We decided to exclude the sample with 7 at. % of Al from the fitting process. There are several reasons why to do that: structural investigations indicate that the sample with 7 at. % of Al is qualitatively different [16], all magnetic characteristics (magnetic moment, Curie temperature, hyperfine magnetic fields) are significantly reduced. The fitting process then gave a value of D_0 = 0,03 ± 0.2 meVnm^2 which is very close to zero (Fig. 2). This indicates that the FeAlNbCuSiB alloys with Al concentration up to 5 at. % of Al we can consider as Heisenberg ferromagnets with a possible very slight extension of the exchange interaction beyond the nearest-neighbour distance.

Annealed samples: During the annealing of the FeAlNbCuSiB samples the most of Al enters the nanograins and the a–Fe(Si,Al) phase crystallizes, however, some Al remains in the amorphous matrix [6,17,4]. The observed decrease of the magnetic moment is caused by dilution effect in the grains. The kink in the dependence at 5 at. % of Al is very probably the consequence of structural ordering [15]. The best, almost ideally ordered DO3 structure of the crystalline phase was detected by Mössbauer spectrometry just in the samples with 5 at. % of Al [6,18,19]. Opposite to the FeAlNbCuSiB samples, in the annealed FeAlZrB series the concentration of Al in the Zr-enriched amorphous intergranular phase is generally higher than that in the α–Fe nanocrystalline phase [8]. The dilution effect in the grains becomes visible only at high Al concentrations, and the initial increase of magnetic moment up to 3-5 at. % of Al reflects the effect of Al in the amorphous matrix discussed above in the case of as-quenched samples.

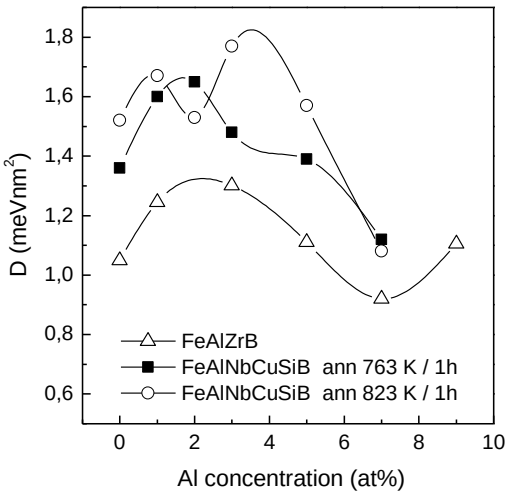

Fig. 4 Concentration dependence of the spin-wave stiffness constant for the annealed samples.

The concentration dependence of the spin-wave stiffness constant reflects an initial exchange hardening for lower concentrations followed by softening at higher concentrations of Al (Fig. 4). As we have a two-phase material we have to take into account at least two processes which affect the magnetic interactions in the alloy: (i) processes in the nanocrystalline grains and (ii) processes in the intergranular residual amorphous phase. In FeAlZrB samples, as it was mentioned before, during the crystallization process the Al atoms are attracted by the Zr atoms, thus they remain in the Zr-enriched amorphous phase [8]. We suppose that small amount of Al, below 3 at. %, suppresses the superexchange interactions, preferably on the grain boundaries, and enforces the long-range interaction between the bcc Fe nanocrystals, what causes a hardening of the exchange interaction. Further increase of the Al content leads probably to solution of some Al in the bcc Fe grains. This fact causes the softening of the exchange interaction.

4. CONCLUSION

The influence of aluminium substitution for iron on the magnetic properties of amorphous and nanocrystalline Finemet and Nanoperm type alloys ($Fe_{73.5-x}Al_xNb_3Cu_1Si_{13.5}B_9$, x = 0, 1, 2, 3, 5 and 7 at. % and $Fe_{88-x}Al_xZr_7B_5$, x = 0, 1, 3, 5, 7 and 9 at. %, respectively) was investigated.

The low-temperature thermomagnetic curves were found to obey the Bloch's $T^{3/2}$ law, for both series of samples.

The dependence of the spin-wave stiffness constant D on the Curie temperature $T_{C\mathrm{am}}$ for as quenched samples follows a relation $D = D_0 + mT_C$ with $D_0 = 0.03 \pm 0.2$ and -0.46 ± 0.1 meVnm^2 for FeAlNbCuSiB and FeAlZrB samples, respectively. These values imply that the FeAlNbCuSiB alloys are very close to Heisenberg type of ferromagnets with direct exchange interactions confined to the nearest neighbours only, whereas in the FeAlZrB alloys superexchange antiferromagnetic interactions play role, resulting in the asperomagnetic spin structure of the alloy. Concentration dependence of the Curie temperature and spin-wave stiffness constant supports this conclusion, as they are monotonously increasing for FeAlZrB alloys, reflecting the exchange hardening due to Al that suppresses the asperomagnetism in the alloy. The same dependences are slightly increasing only for small Al concentration in the FeAlNbCuSiB alloys, for which the noncollinear spin structure is not typical. Concentration dependence of magnetic moment reinforces as well the ordering influence of Al on the noncollinear spin structure in the FeAlZrB alloy.

In the annealed samples the same influence of Al in the intergranular phase can be observed together with the dilution effect in the nanocrystalline grains.

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BIOGRAPHY

Anna Zorkovská was born on 10.2.1962. She graduated with distinction from the Faculty of Science, University of P.J. Šafárik in Košice. She has been working at the Department of Experimental Physics since 1986. Her scientific research is focused on the amorphous and nanocrystalline soft magnetic alloys, especially on the relationship between their structure and magnetic properties. She defended her PhD. thesis on the „Influence of substitutions on the structure and magnetic properties of Finemet“ in 2001.