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MAGNETIC PROPERTIES OF BALL-MILLED Fe-RICH $Fe_{50+x}Al_{50-x}$ ALLOYS

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Abstract. The results of Mössbauer spectroscopy and magnetization measurements on Fe-rich $Fe_{50+x}Al_{50-x}$ (x=0 to 10) alloys with B2 structure, ball-milled and postannealed at 450K, are reported. This sample preparation procedure results in a grain size around 8 nm and a special grain structure where most of the magnetic Fe atoms can be found in the grain boundaries. The thickness of the magnetic boundary region is increasing with the amount of excess Fe. A sudden decrease of the magnetic anisotropy is observed between x=6 and 8.

Ordered, stoichiometric FeAl has a CsCl-type (B2) structure where each Fe atom has 8 Al nearest and 6 Fe next nearest neighbours. It is nonmagnetic, the Fe atoms have no localized magnetic moments. In Fe-Al alloys with the bcc structure the magnetic moments of the Fe atoms depend strongly on the local environments. As a rule, Fe atoms with less than four nearest Fe neighbours possess no localized magnetic moments, and the Fe atoms become magnetic when they have four or more Fe nearest neighbours. The magnetic moment of Fe atoms with five or more Fe neighbours is about the same as in pure α-Fe (2.2 μ_B), and about 20% lower in the 4Fe - 4Al environments [1,2]. This trend means that Fe atoms in off-stoichiometric Fe-Al alloys with excess Fe atoms sitting on Al sites have magnetic moments and the number of magnetic Fe atoms can be considerably increased in disordered alloys, or after cold working or ball-milling which result in the formation of antiphase boundaries (APB's) [3,4].

It has been shown [5] that ball-milling of stoichiometric FeAl results in nano-size nonmagnetic grains with ferromagnetic antiphase grain boundaries consisting of about two mono-layers of Fe. The magnetic behaviour of this rigid magnetic foam-like material was found to be uncommon: (i) the transition to the paramagnetic state was glass-like and the relaxation of the magnetic moments was found at rather low temperatures; (ii) the magnitude of the local magnetic moments decreased linearly with increasing temperature and (iii) in large magnetic fields a strongly anisotropic ferromagnetic behaviour was observed. Now these investigations are extended to the case of Fe-rich FeAl alloys where an increase of the thickness of the magnetic boundary region and a transition from a 2D-like to the bulk magnetic behaviour is expected.

The off-stoichiometric $Fe_{50+x}Al_{50-x}$ (x=0 to 10) ingots were prepared from the pure components by induction melting in a cold crucible. X-ray diffraction and low temperature Mössbauer measurement confirmed the well-ordered B2 state. The mechanical milling was carried out in a vibrating frame single ball vessel with a hardened steel ball under continuous pumping by a turbomolecular system. The typical pressure was 10^{-2} Pa. In the present work the samples were ball-milled for 100 h and annealed at 450K. The ball-milling had two effects: it caused disordering of the B2 structure

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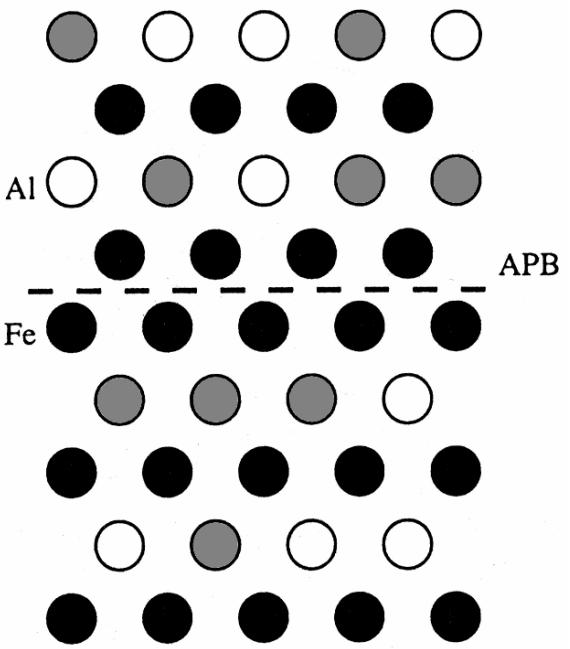

Fig. 1. Schematic picture of the structure of the grain boundary in off-stoichiometric FeAl alloys. Empty circles and dots correspond to Al and Fe atoms on the regular B2 sites, gray circles are the excess Fe atoms on Al sites. The broken line signs the antiphase grain boundary (APB).

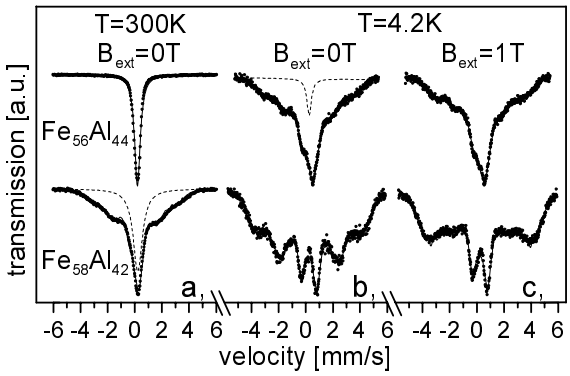

Fig. 2. Transmission Mössbauer spectra of ball-milled (100 h) and annealed (450K) $Fe_{56}Al_{44}$ and $Fe_{58}Al_{42}$ samples measured at room temperature (a) and at 4.2K in 0 T (b) and 1 T (c) external magnetic field directed perpendicularly to the sample plane. The dotted lines are the single line components of the spectra.

and decrease of the grain size. The grain size was about 8 nm after 100 h vibrating-table ball-milling. Annealing of the powders in a Perkin-Elmer Differential Scanning Calorimeter at 650-700K restored the original well-ordered B2 state and increased the grain size to about 20 nm. During this procedure no detectable composition change or contamination occurred since in the case of the stoichiometric sample (x = 0) the narrow single line Mössbauer spectrum characteristic of ordered FeAl was retained. Annealing at 450K did not influence the starting 8 nm grain size but removed the disorder and restored the B2-type ordered state inside the grains.

Transmission ^{57}Fe Mössbauer spectra between 4.2 and 300K, and in external magnetic fields were recorded by a standard constant acceleration spectrometer using a 50 mCi ^{57}Co*Rh* source at room temperature. The magnetic field was applied parallel to the γ-beam, perpendicularly to the sample surface using a 7 T Janis superconducting magnet. Standard procedures were used for the evaluation of the spectra. The magnetisation measurements were performed using a Quantum Design MPMS-5S SQUID magnetometer with a maximum field of 5 T.

Fig. 1 depicts schematically the atomic structure in the grain boundaries of these Fe-rich Fe-Al alloys. Beside the two monolayer thick magnetic Fe antiphase boundary (APB) (in the stoichiometric case each Fe atom has 4 Fe and 4 Al nearest neighbours in these planes), the excess Fe atoms sitting on the Al sites in the neighbourhood of these planes will also have magnetic moments. This results in an irregular increase of the thickness of the magnetic grain boundaries, which was two monolayer thick in the starting stoichiometric case. The number of magnetic Fe atoms increases with increasing Fe concentration, as well as, the magnitude of the magnetic hyperfine splitting (due to both the larger Fe magnetic moment and the higher Fe coordination via the transfer hyperfine field contribution).These are illustrated in the Mössbauer spectra of Fig. 2b. Nonmagnetic Fe atoms have either a single line contribution in the spectra or a small transfer hyperfine field originating from surrounding magnetic Fe atoms. The samples are nonmagnetic at room temperature for $x \leq 6$, as it is indicated by the narrow single line spectrum for $Fe_{56}Al_{44}$ in Fig. 2a but the absence of magnetic splitting can also be due to a superparamagnetic

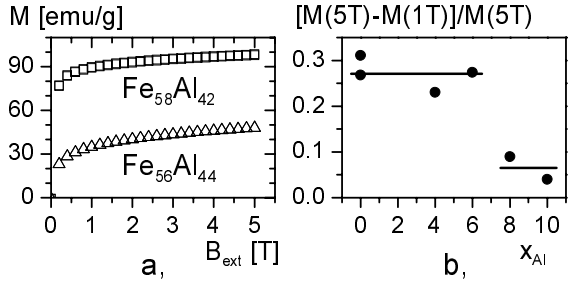

Fig. 3. 5K values of the magnetization, *M* vs. the applied magnetic field for $Fe_{56}Al_{44}$ and $Fe_{58}Al_{42}$ ball-milled (100 h) and annealed (450K) samples (a) and the reduced differences between the 5 T and 1 T values, (*M*(5 T)-*M*(1 T))/*M*(5 T) as a function of the excess Fe content (b).

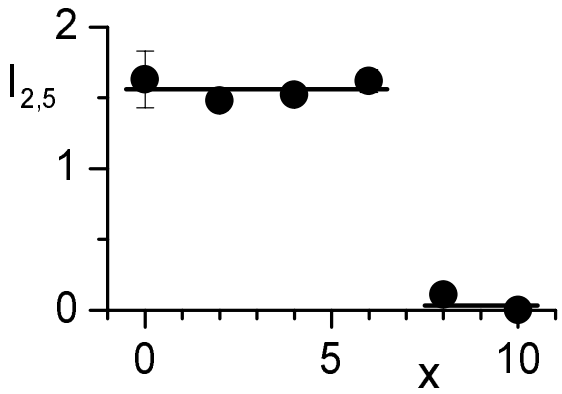

Fig. 4. Intensity of the second and fifth lines of the Mössbauer spectra, $I_{2,5}$ for $Fe_{50+x}Al_{50-x}$ ball-milled (100 h) and annealed (450K) alloys, measured at 4.2K in 1 T external magnetic field directed perpendicularly to the sample plane.

behaviour, as it was shown in more details [6] for ultrathin Fe/Al multilayers. When the spectra taken at room temperature and 4.2K (i.e. above and below the blocking temperature of the superparamagnetic particles) are compared, it is well seen that the single line component present in the samples at room temperature is small (dotted component in Fig. 2b) or not even detectable ($Fe_{58}Al_{42}$ sample) at 4.2K.

Typical magnetization curves measured at 5K as a function of the applied field are shown in Fig. 3a. A typical feature of these curves is that they cannot be saturated even in 5 T. A significant change in the high field slope of the magnetization curves can be observed as the amount of excess Fe is increasing. It can be characterized with the reduced difference: (*M*(5 T) - *M*(1 T))/*M*(5 T), where *M* is the magnetization measured at the respective magnetic field. This quantity is shown in Fig. 3b as a function of the sample composition and it shows a sudden decrease between x=6 and 8.

It is difficult to separate the contribution of Pauli paramagnetism and highly anisotropic ferromagnetism in the magnetization curve: both contributions result in unsaturated magnetic behaviour in applied fields. However, information on the direction of the Fe magnetic moments is given by the relative intensity of the second and fifth lines (corresponding to the $\Delta m = 0$ nuclear transitions), $I_{2,5}$ of the magnetically split Mössbauer spectra. $I_{2,5} = 4\sin^2\theta/(1 + \cos^2\theta)$, where θ is the angle between the magnetic moment and the magnetic field B_{ext} applied parallel to the γ-beam direction. $I_{2,5} = 2$ corresponds to a random Fe spin orientation and this value was found without an applied field (Fig. 2b). For complete saturation, *i.e.* in the case when all the magnetic moments are collinear to B_{ext}, $I_{2,5} = 0$. Fig. 4 shows the values of $I_{2,5}$ measured at 4.2K in 1 T as a function of the excess Fe content. For $x \leq 6$ the applied magnetic field has little influence on the direction of the Fe magnetic moments. Similar strong magnetic anisotropy was reported for ferromagnetic clusters along the APB in off-stoichiometric Fe-Al alloys [3] and for magnetic grain boundaries of the stoichiometric alloy [5]. Increase in the thickness of the magnetic region, i.e. in the amount of excess Fe, results in a sudden decrease of the $I_{2,5}$ values measured in 1 T. This behaviour is well demonstrated in Fig. 2c, where the shape of the spectrum shows practically no change for $Fe_{56}Al_{44}$, while in the case of $Fe_{58}Al_{42}$ a significant decrease in the intensity of the second and fifth lines is observed for the applied 1 T external field. It signifies an abrupt decrease of the magnetic anisotropy for the increase of the magnetic layer thickness.

In conclusion, a sudden decrease of the strength of the magnetic anisotropy is observed in ball-milled and postannealed (at 450K) off-stoichiometric FeAl alloys as a function of the excess Fe content. The low temperature Mössbauer spectra reveal that it is not connected to the

superparamagnetic behaviour observed at room temperature. The decrease of the magnetic anisotropy is attributed to a transition from the behaviour expected for two monolayer thick Fe layers to the behaviour characteristic of bulk three dimensional alloys.

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