Investigations of magnetism and domain wall in ferromagnetic amorphous alloy  $Co_{90}Zr_{10}$ 

The first results of studies on the crystallization and domain structure and on the magnetic properties of the amorphous metallic alloy  $Co_{90}Zr_{10}$  have been reported in [1, 2]. The present description of the properties of the cross-tie type domain wall forms a small part of studies on the effect of annealing on the domain structure and domain wall energy in the amorphous alloy  $Co_{90}Zr_{10}$ .

Co<sub>90</sub>Zr<sub>10</sub> was obtained by arc melting and transformed to the amorphous state by continuous casting onto a rotating cylindrical surface. The resulting ribbon, about 2.5 mm wide and  $20 \mu \text{m}$ thick, was thinned by two-sided electrochemical polishing (Struers) with electrolyte Struers A8 at 258 K. Component  $M_{sv}$  of saturation magnetization was determined by Lorentz transmission electron microscopy (LEM) using Foucault's contrast, whereas the domain structure was observed in Fresnel's contrast [3]. Observations were made during heating of the preparation in a Philips EM 300 microscope, using a heating holder. Values of magnifications M and of the out-of-focus distances z, given in the domain-wall pictures, were determined by photographing of the carbon grid, with parameter amounting to 1135 lines mm<sup>-1</sup>. Domain wall width was calculated according to Wade [4], i.e.  $\delta_{w} = (\delta_{wd} - \delta_{wc})/2$ , where  $\delta_{w}$  is the domain wall width,  $\delta_{wd/c}$  is the width of the divergent/ convergent wall, being sufficiently accurate for out-of-focus distances of an order of a few millimeters. To improve the accuracy of the  $\delta_{wd}$  and  $\delta_{wc}$  measurements, microphotometric analysis of negative pictures of the domain wall was applied. The theoretical values of magnetization as a function of temperature, described by Brillouin's function in reduced co-ordinates  $\sigma(\tau)$ ,  $\sigma = M(T)/M(0 \text{ K})$ ,  $\tau = T/T_c$ , were calculated using a Hewlett– Packard minicomputer.

Studies of amorphous ferromagnetic alloy  $Co_{90}Zr_{10}$  by the Weiss-Forrer method [2] showed that the easy magnetization direction lies in the ribbon plane,  $\theta = 90^{\circ}$  (Fig. 1); magnetization saturation,  $M_s$ , at room temperature equalled 1086 G and the anisotropy constant,  $K = 0.15 \text{ J} \text{ cm}^{-3}$ . Fig. 2 shows the diffraction pattern from the domain wall region at about 300 K; the straight streak connecting the spots indicates that in fact the Bloch wall is involved. As a result of the action of the Lorentz force, the central beam is deflected by an angle  $\psi = 2.6 \times 10^{-4} \text{ rad}$ , determined from the known microscope constant  $\lambda L. M_{sy} = 1100 \text{ G}$  was determined, with a 5% error from the equation [5]

$$\psi = \frac{e\lambda}{h} \times 4\pi M_{\rm sy} t,$$

where e is the electronic charge,  $\lambda$  is the electron wavelength at 100 kV,  $M_{sy}$  is the component  $M_s$ lying in the layer plane and t is the layer thickness  $\approx 2100$  Å. Thus, it can be assumed that the vector



Figure 1 Domain structure model;  $\theta$  and  $\phi$  respectively, represent the deflection of easy magnetization axis and of magnetization vector  $\overline{M}_s$  from the normal to the layer plane.

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Figure 2 Deflection of electron beam within the domain wall region in the amorphous alloy  $Co_{90}$ Zr<sub>10</sub>,

 $M_s$  lies in the layer plane consistent with the easy axis direction,  $\phi = \theta = 90^\circ$  (Fig. 1). A certain deflection of vector  $\overline{M}_s$  from the easy direction, caused by a change in the edge conditions, may only occur near the ribbon edge. This effect has no influence on the results obtained for domain walls lying further from the ribbon edge.

Theoretical calculations performed for thin crystalline layers [6] have shown that the effect of layer thickness on the value of  $\phi$  is negligible, if

 $\theta$  tends to 90°, i.e. if the easy direction lies in the layer plane. A small or zero value of angle  $(\theta - \phi)$ , i.e. a concordant direction of vector  $\overline{M}_s$  and of the easy axis, is also supported in the paper by Malek and Kambersky [7], only if  $K < 2\pi M_s^2$ ; this inequality is satisfied for the material studied.

In this study application was made of the simplest approximation of the effective field, which consists of the consideration of a single atom, and all interactions of this atom with the remaining ones are substituted by the action of the effective field. The assumption that the effective field is proportional to the mean real magnetic moment of the crystal leads to a simplification of the Hamiltonian,  $\mathcal{H}$ , of Heisenberg's exchange

$$\mathcal{H} = -2 \sum_{i < j} J_{ij} S_i S_j, \qquad (1)$$

where  $J_{ij}$  is a function of relative distance  $R_i - R_j$ , giving

$$\mathcal{H} = -2JS_i \sum_{j=1}^{2} S_j, \qquad (2)$$

where the summation is taken over the z atoms closest to the *i*th atom. This model is often used for the description of the magnetic properties of materials with short-range order, these also include amorphous alloys [8, 9]. The function M(T) in



Figure 3 Changes in magnetization as a function of temperature in reduced co-ordinates,  $\sigma(\tau)$ . Theoretical plots (continuous lines) described by Equation 4 for spin values S = 1/2, and for various values of the fluctuation of the exchange integral, as well as the experimental plot (broken line), are shown.



reduced co-ordinates  $\sigma(\tau)$  is described by Brillouin's function,

(c)

$$B_{s}(X) = \frac{2S+1}{2S} cth \left[ \left( \frac{2S+1}{3S} \right) X \right] - \frac{1}{2S} cth \left( \frac{X}{2S} \right)$$
(3)

into which  $X = [(3S/S + 1)\sigma/\tau]$  was substituted [10]. The value  $\sigma$  is thus the variable which, moreover, takes into account the possibility of fluctuation of the exchange integral by the introduction of factors  $1 + \Delta$  and  $1 - \Delta$ , so that

 $\sigma = \frac{1}{2} \{ B_{s}[X(1+\Delta)] + B_{s}[X(1-\Delta)] \}.$ (4)

Fig. 3 shows the experimental plot  $\sigma(\tau)$  and the theoretical curves for S = 1/2, described by Equation 4 satisfied with an accuracy better than  $\pm 0.001\sigma$ . On this basis, the fluctuation of the exchange integral in amorphous alloy  $Co_{90}Zr_{10}$  was assumed to be  $\Delta = 0.2$ , as being nearest to this theoretical curve, although at temperatures ranging from 0.4 to  $0.7\tau$ , the value of  $\Delta$  is closer to 0.25.

An amorphous foil  $Co_{90}Zr_{10}$  sample was heated from 310 to 650 K, with simultaneous observations of a fragment of the cross-tie structure (Fig. 4a



Figure 4 a and b Cross-tie domain wall in the amorphous alloy  $Co_{90}Zr_{10}$  at 310 K (Lorentz microscopy), magnifications (a) × 8860, (b) × 8340, out-of-focus distances (a) z = 4.9 mm, (b) - 2.6 mm. A is the site of measurement of  $\delta_{w}$ , and B is the Bloch line. (c) Diffraction from the region shown in Fig. 4a and b after completion of the experiment, i.e. at T = 650 K.

and b). After completion of the experiment, the foil remained in an amorphous state (Fig. 4c). Fig. 5 presents the changes in half-width of the crosstie domain wall, measured at site A (Fig. 4a) at various temperatures between 310 and 650 K. Moreover, Fig. 4a shows the Bloch line at B. The cross-tie wall comprises segments magnetized alternately in the opposite directions, because spins have a dextro- or levorotatory orientation. In this way the magnetostatic energy in the wall is reduced. These segments are separated by Bloch lines and cross-walls. In the investigated amorphous foils the layer thickness, t, exerted a very slight effect on



Figure 5 Changes in cross-tie domain wall width  $\delta_{\mathbf{w}}$  (Fig. 4a and b) during heating of the amorphous foil  $\operatorname{Co}_{90}Zr_{10}$ ,  $\delta_{\mathbf{w}} = (\delta_{wd} - \delta_{wc})/2$ .

the domain wall width, only if t > 1000 Å. A similar effect has been observed in crystalline foils of h c p Co [6], with angle  $\theta$  near 90°.

Near 500 K, the width of the cross-tie wall is minimal and approaches the values typical of thin crystals of h c p Co. Changes in domain wall width are caused by a change in energy which in this case mainly comprises the exchange energy and anisotropy energy. Magnetostriction energy, which is much lower, is neglected because the first measurements pointed to a very low value of  $\lambda_s$  in the amorphous alloy Co<sub>90</sub>Zr<sub>10</sub>; it is assumed that the magnetostatic energy,  $E_{me} = 0$  for a 180° Bloch wall.

To summarize, for the amorphous ferromagnetic alloy  $\text{Co}_{90}\text{Zr}_{10}$  the localization of vector  $\overline{M}_s$  which proved to be consistent with the easy axis was determined, and the fluctuation,  $\Delta$ , of the exchange integral was evaluated to be 0.2. The effect of temperature on the cross-tie domain wall width,  $\delta_w$ , which has a minimum at about 500 K was demonstrated.

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## Formations of rhombohedral boron nitride, as revealed by TEM—electron energy loss spectroscopy

Boron nitride crystallizes at atmospheric pressure in a graphite-like layered structure called hexagonal (or h-) BN [1], but the form of stacking of successive layers is different for h-BN compared with graphite; i.e. the hexagons in the honeycomb network lie parallel to the *c*-axis in h-BN but are oblique in graphite. From these packing characteristics, the presence of rhombohedral  $\beta$ -graphite is naturally expected but that of h-BN not because, as Pease [1] first pointed out, in order to take the rhombohedral (or r-) BN form, the spatial relations between the two nearest layers must be changed

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from those in h-BN. In fact, reliable experimental data on r-BN have not so far been presented; it has only been reported that in powder X-ray diffraction of a fusion product of KCN and  $Na_2B_4O_7$  some peaks can be indexed as r-BN [2]. In the present note, however, we present more reliable experimental data on the existence of r-BN, by the combination of transmission electron microscopy (TEM) and qualitative microanalyses by electron energy loss spectroscopy (ELS).

The samples were prepared by deposition at  $1500^{\circ}$  C from h-BN vapour originally formed at  $2100^{\circ}$  C in a graphite-resistance tube-furnace [3]. The products were collected on a pitted carbon film and examined by an ordinal TEM (H-500 type,