Magnetic hysteresis and crystallization studies on metallic glass alloy $\text{Fe}_{67}\text{Co}_{18}\text{B}_{14}\text{Si}_1$

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Abstract. Magnetic hysteresis studies were carried out on Metglas 2605 Co($\text{Fe}_{67}\text{Co}_{18}\text{B}_{14}\text{Si}_1$) samples, cut parallel and perpendicular to the ribbon axis and annealed at different temperatures. The samples annealed at 450°C for 2 hr show a coercive force of 8.75 Oe and 0.60 Oe in the parallel and perpendicular directions respectively. Electron probe micro analysis studies revealed the onset of primary crystallization at 400°C and a gradual displacement of B and Si from the lattice as the annealing temperature was increased to 450°C. The observed large coercive force is due to an increase in anisotropy resulting from an intergrowth pattern of the type $\text{Fe}_x\text{Co}_{1-x}$, $0.3 < x < 1.0$, including boron containing phases such as $(\text{FeCo})\text{B}$, $(\text{FeCo})_2\text{B}$, $(\text{FeCo})_3\text{B}$, developed by the displacement of B and Si from the original amorphous lattice.

Keywords. Amorphous alloys; anisotropy; crystallization; magnetic hysteresis.

1. Introduction

Recently, amorphous alloys have emerged as a new class of materials for constituting high performance transducers and sensors. Both isotropic and anisotropic properties of amorphous alloys find applications in device construction (Mohri 1984; Sasada *et al* 1984). The material under study, commercially known as Metglas 2604 Co with the composition $\text{Fe}_{67}\text{Co}_{18}\text{B}_{14}\text{Si}_1$, has a high magnetostriction constant ($\lambda = 35 \times 10^{-6}$) (Allied 1981) coupled with a higher saturation induction and is suitable for underwater transducer applications (Mohri 1984). The magnetic properties of this material could be conveniently modified by adopting suitable annealing procedures. The magnetic hysteresis properties, crystallization aspects and its relation to magnetic anisotropy of this material annealed to different temperatures have been reported in this paper.

2. Experimental

Metglas 2605 Co ribbon, 50 mm wide, 27 μ thick (supplied by Allied Corporation, USA) was cut into strips of dimensions 50 mm $\times$ 4 mm and of equal weight, both parallel and perpendicular to the ribbon axis. These were annealed at 100, 200, 300, 400 and 450°C for a constant period of 2 hr.

Hysteresis studies were carried out on the strip samples using a hysteresis loop tracer (Radhakrishnamurthy *et al* 1978) suitably modified to minimize the demagnetization effects. The coercive force H_c measured on the original sample is 0.08 Oe, which corresponds well with the value given in the specification of this material. The crystallization and composition analysis were carried out using an

electron probe micro analyser (model: Camebax, Chemica, France) (Beaman and Isasi 1972). Phase analysis, if any, was carried out using a Siemens Kristalloflux x-ray diffractometer. The statistical data on the crystallite dimensions were obtained using a TAS plus image analyser.

3. Results and discussion

Figures 1(a) to (f) depict the hysteresis of the Metglas samples taken parallel to the ribbon axis and annealed for 2 hr at temperatures (a) as obtained, (b) 100°C, (c) 200°C, (d) 300°C, (e) 400°C and (f) 450°C. The hysteresis loops for samples taken perpendicular to ribbon axis are shown in figures 2(a) to (f). The H_c data are presented in table 1.

From figures 1(a) and 2(a) a slight difference is seen in the H_c of the original sample in either direction. It can be inferred, therefore, that the starting samples possess little anisotropy due to magnetostriction and/or magnetoelastic effects (Haregawa 1976; Suja *et al* 1975; Takahashi *et al* 1976). Samples annealed at 400°C have shown clusters of tiny crystallites (figure 3a), without a significant change in the magnetic hysteresis (figures 1e and 2e). The crystallite dimensions range from a few hundred to about a thousand Angstroms. Due to their small size such small crystallites formed with the onset of crystallization may be considered as single domain regions (Chaugule *et al* 1983). At 450°C these crystallites coalesce to form into narrow regions of nearly 50–100 μ length and about 10 μ width (figure 3b). The hillock type crystallization products show a regular pattern elongated perpendicular to the ribbon axis. Texture Analysis System (TAS) image analysis revealed that the form factor of the regions is about 0.528 with an equivalent diameter of about 107 μ .

3.1 X-ray diffraction studies

X-ray diffraction analysis revealed a consistent amorphous structure with the samples annealed at 100, 200, 300 and 400°C. The sample annealed at 450°C shows a distinct crystalline diffraction pattern with d -values at 2.03, 1.43 and 1.17 Å. A variety of phases such as α -Fe, $\text{Fe}_x\text{Co}_{1-x}$, (FeCo)B, $(\text{FeCo})_2\text{B}$, $(\text{FeCo})_3\text{B}$ are expected (Baburaj *et al* 1985; Harold and Kosten 1978; Takacs *et al* 1975). Thus the observed XRD lines possibly belong to some of these phases. Further, distinct regions of α -Fe or (FeCo) type phases were not identified in the electron probe analysis (see table 2), suggesting that these could be intergrowth regions of submicron dimensions.

3.2 Electron probe micro analysis

Electron probe micro analysis was carried out at nearly 20, 40, 60 and 80 μ distance from one end to the other for several crystallites. The percentage composition of

Figure 1. Hysteresis loops of Metglas 2605 Co parallel to the ribbon axis. Annealing temperatures (a) As obtained, (b) 100°C, (c) 200°C, (d) 300°C, (e) 400°C, (f) 450°C. Scale: X-axis (a) to (e) one big division = 2.5 Oe and for (f) it is 3.5 Oe.

Figure 1. For caption, see page 568

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Figure 2. For caption, see page 573.

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Table 1. Coercive force H_c of Metglas 2605 in the directions parallel and perpendicular to ribbon axis.

Annealing temperature (°C)	Coercive force (Oe)	
	Parallel	Perpendicular
30	0.08	0.15
100	0.08	0.15
200	0.15	0.20
300	0.30	0.30
400	0.35	0.35
450	8.75	0.60

Fe, Co, Si was obtained against calibrated standards with a statistical accuracy of 0.5% of the measured value and B concentration was obtained by calculating the difference. The error estimated is about +1% of the measured concentration (Beaman and Isasi 1972; Heinrich 1981). The results show a significant spatial variation in composition as given in table 2. These results indicate that the crystals are boron-deficient at its centre. When there is a gradual increase in boron content away from the centre the composition around the periphery of the crystals is enriched in boron and silicon. Also, there seems to be a preferential rejection of boron at the first instance when compared to that of silicon as inferred from the Si enrichment at 20 and 80 μ (see table 2). The crystallization process could therefore be categorized as the primary crystallization (Baburaj *et al* 1985; Harold and Koster 1978; Takacs *et al* 1975) which involved preferential displacement of boron followed by silicon into the amorphous matrix. Distinct regions of iron have not been observed suggesting that the α -Fe phase identified in x-ray diffraction study could be possibly present as intergrowth regions of submicron dimensions during the primary crystallization process.

3.3 Magnetic anisotropy

The hysteresis loops for the samples annealed at 450°C (figures 1f and 2f) show enhanced anisotropic effects. H_c increased to a value of 0.60 Oe perpendicular to the ribbon axis, while it is 8.75 Oe in the parallel direction. However, the sample annealed at 400°C showed an H_c value of 0.35 Oe in either direction (figures 1e and 2e), despite the fact that microcrystalline regions appeared due to the onset of crystallization (figure 3a). The composition of such crystallites is, therefore, expected to be nearly the same as that of the bulk. The crystallization may proceed through the formation of intergrowth structures with complex repeat sequences (Rao 1985) that are possible with the evolution of textures based on Bernal polyhedra (Finney and Wallace 1981). Further, as seen in figure 3b the hillock regions are elongated perpendicular to the long axis of the ribbon. The hysteresis loops in figures 1f and 2f reveal that the hard axis of the 450°C annealed ribbon lies in a direction parallel to the ribbon axis. These results suggest that the intergrowth pattern is likely to occur in a direction perpendicular to the long axis of the hillock structure which, in turn, indicates that the intergrowth patterns are parallel to the ribbon axis.

Figure 2. Hysteresis loops of Metglas 2605 Co perpendicular to the ribbon axis. Annealing temperatures (a) As obtained, (b) 100°C, (c) 200°C, (d) 300°C, (e) 400°C, (f) 450°C. Scale: X-axis—one big division = 2.5 Oe for (a) to (f).

Figure 3. (a) Microcrystallites formed at 400°C. Scale: the bar represents 10 μ . (b) Hillock type crystallization formed at 450°C. Scale: the larger rectangle represents 100 μ . Arrow indicates the direction of the ribbon axis.

In accordance with the recent Mössbauer investigations (Bhatnagar *et al* 1985) and in the wake of preferential rejection of boron and silicon, we propose that the intergrowth regions may comprise of compositions of the form $\text{Fe}_x\text{Co}_{1-x}$, ($0.3 < x < 1.0$), α -Fe including the boron-containing phases $(\text{FeCo})\text{B}$, $(\text{FeCo})_2\text{B}$, $(\text{FeCo})_3\text{B}$ preferentially grown parallel to the ribbon axis. The compositions $\text{Fe}_x\text{Co}_{1-x}$, with $0.3 < x < 1.0$ were known to be strongly anisotropic with anisotropic constant K for α -Fe, $\text{Fe}_{0.7}\text{Co}_{0.3}$ and $\text{Fe}_{0.3}\text{Co}_{0.7}$ being 460, -430 and 102 respectively in units of $\times 10^{-3} \text{ erg/cm}^3$ (Gray 1963). Thus the observed anisotropy may be attributed to the presence of compositions of the type α -Fe, $\text{Fe}_{0.7}\text{Co}_{0.3}$,

Table 2. Typical composition of a crystallite from end to end—EPMA data.

Element	Composition from one end at (μ)			
	20	40	60	80
Fe	73.37	75.99	75.49	70.10
Co	20.16	20.56	20.36	19.22
Si	1.01	0.92	0.67	1.14
B By difference	5.46	2.53	3.47	9.54

Note: Fe, Co and Si were estimated against calibrated standards and B concentration was obtained by difference. Estimated error is of the order of $\pm 1\%$ of the measured value.

$\text{Fe}_{0.3}\text{Co}_{0.7}$ and FeCo among the various compositions that appear as intergrowth regions preferentially formed parallel to the ribbon axis.

4. Conclusions

(i) Thermal annealing of Metglas 2605 Co at 450°C leads to pronounced magnetic anisotropy with respect to ribbon axis. (ii) The thermally-induced anisotropy of Metglas 2605 Co samples could be explained on the basis of the intergrowth patterns formed preferentially parallel to the ribbon axis leading to local compositions of the type $\alpha\text{-Fe}$, $\text{Fe}_x\text{Co}_{1-x}$, ($0.3 \leq x \leq 1.0$), FeCo, (FeCo)B, $(\text{FeCo})_2\text{B}$, $(\text{FeCo})_3\text{B}$ etc.

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