Structural and magnetic study of nitrated $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$ and $\text{Co}_{74}\text{Fe}_4\text{Mn}_4\text{B}_{12}\text{Si}_6$ ribbons

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Abstract. The nitriding thermochemical treatment (NTT) is commonly used for steels. In this paper, the experimental conditions required for NTT, and the influence of such treatments on the structure and hysteresis loops of $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$ and $\text{Co}_{74}\text{Fe}_4\text{Mn}_4\text{B}_{12}\text{Si}_6$ ribbons are reported. The results have been compared with those obtained with ribbons treated according to conventional thermal treatment (CTT) as well.

Keywords. NTT; $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$; $\text{Co}_{74}\text{Fe}_4\text{Mn}_4\text{B}_{12}\text{Si}_6$.

1. Introduction

Cobalt-based amorphous alloys are of interest in high-frequency applications. The presence of manganese, even at low concentrations, leads to an increase of magnetization of such alloys and shifts the crystallization temperature beyond the Curie temperature (Handley and Sullivan 1981; Obi *et al* 1981).

Co–Fe–B–Si and Co–Fe–Mn–B–Si amorphous alloys are not only ferromagnetic at room temperature but possess interesting magnetostrictive property as well. While the magnetostriction changes from negative to positive values versus the Fe concentration (Madurga *et al* 1985), the Mössbauer spectra of such alloys show that the Fe moment increases with increasing Co concentration (Krishnan *et al* 1985). Moreover, calorimetric studies show that such materials exhibit good thermal stability (Atmani *et al* 1995).

Thermochemical treatments are commonly used in the steel industry. These treatments act by thermal diffusion of one or more external elements. In nitriding treatment, the element used is nitrogen which results in the improvement of some mechanical properties (Muzart *et al* 1993; Iacob *et al* 1994). However, there is no reported literature available on the nitrated ribbons.

In this paper, the experimental condition required for nitriding thermochemical treatment have been reported by us, in particular, we have studied the feasibility of such a treatment for magnetic ribbons. Results on the structure and the hysteresis loops obtained with $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$ and $\text{Co}_{74}\text{Fe}_4\text{Mn}_4\text{B}_{12}\text{Si}_6$, crystallized by conventional treatment as well as by nitriding treatment, have been presented.

2. Experimental

Amorphous $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$ and $\text{Co}_{74}\text{Fe}_4\text{Mn}_4\text{B}_{12}\text{Si}_6$ ribbons were prepared by the single-roller melt technique. The ribbons were 3 mm wide and about 30 μm thick.

In order to carry out thermochemical treatments of the samples, a fluidized bed homemade furnace was used which was modified for the classical nitriding thermochemical treatments. The gas used was ammonia (NH_3), at variable flow rate (from 0.1–0.7 $\text{m}^3\text{N/h}$) and pressure at 2×10^5 Pa, showing temperature-dependent dissociation rate. At a temperature equal to or higher than 510°C, ammonia dissociated according to the reaction:

The parameters that contribute to the nitriding thermochemical treatment are temperature, time and nitrogen. To separate the influence of temperature and that of nitrogen, conventional thermal treatments on the ribbons using the same conditions as those used for the nitriding thermochemical treatments were carried out. Thus the samples were treated under the following conditions:

2.1 For nitriding thermochemical treatment (NTT):

Temperature	: 520°C
Time	: 6 h
Pressure	: 2×10^5 Pa
Gas	: Dissociation of $\text{NH}_3 + \text{N}_2$ atmosphere
Rate dissociation	: 0.1 $\text{m}^3\text{N/h}$

2.2 For conventional thermal treatment (CTT)

Temperature	: 520°C
Time	: 6 h
Gas	: Ar atmosphere

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The nitrogen distribution in the sample was checked by electron microprobe analysis (EDAX 9100 Philips). The crystalline phases of the treated samples were checked by X-ray diffraction with Co-K α radiation (INEL CPS 120). The hysteresis loops, at room temperature, were obtained by a vibrating sample magnetometer (VSM).

3. Results

For steels, at each edge of the sample, there is a 100 μm thick domain wherein distribution of the nitrogen follows an exponential law (Iacob *et al* 1994; Thoumire *et al* 1997). Curve a, in figure 1, shows nitrogen distribution in the case of FeSi sheets (1 mm thick) which could be compared with curve b (figure 1), which represents theoretical distribution of nitrogen diffusion in steel. It was presumed that the situation would be different in the case of ribbons which were $\approx 30 \mu\text{m}$ thick, and would perhaps show nitrogen distribution throughout the thickness. Figure 2 shows an example of the profile of nitrogen obtained with a nitrided- $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$ ribbon. It displays homogeneous chemical distribution. The slight asymmetry

Figure 1. a. The profile of nitrogen in an Fe-Si sheet after NTT operation and b. theoretical representation of nitrogen diffusion in a steel.

Figure 2. The profile of nitrogen in a $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$ ribbon after NTT operation.

observed in the profile could perhaps be explained by the difference in the morphology of the two sides of the ribbon, i.e. due to the first side being cooled by conduction over the wheel while the second side is cooled by convection.

Figure 3 shows the results obtained by X-ray diffraction with nitrided samples. The indexation of the peaks enables some nitrides, such as Co_2N and Mn_2N , to be recognized in $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$ and $\text{Co}_{74}\text{Fe}_4\text{Mn}_4\text{B}_{12}\text{Si}_6$ samples, respectively. The peaks appear to be wider compared with those obtained with CTT ribbons. This reflects a smaller grain size in the case of NTT samples.

Figure 4 shows the hysteresis loops obtained with $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$ treated by CTT and NTT (figures 4a and b) and the loop obtained with NTT $\text{Co}_{74}\text{Fe}_4\text{Mn}_4\text{B}_{12}\text{Si}_6$ (figure 4c).

Thus based on the above studies, we can conclude that:

- (i) the coercive field, H_c , for the conventionally-treated $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$ sample is 112 Oe, while the coercive field of an equivalent nitrided sample is 77 Oe. The decrease of the coercive field may be related to the grain size, which is lower in the case of NTT samples;
- (ii) the presence of a small amount of manganese in the alloy also affects the coercive field: the coercive field being 60 Oe;
- (iii) the saturation magnetization values show a decrease when the sample is nitrided. The values are 134 emu/g and 96 emu/g for CTT and NTT, $\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$, respectively.

From models available in the literature, it is possible to propose a law describing the trend for the magnetization against the field. We have used the Gonda model (Gonda *et al* 1984). On the basis of this model, the upper

Figure 3. X-ray diffraction results obtained on nitrided ribbons.

Figure 4. Hysteresis loops obtained with the ribbons subjected to conventional thermal and nitriding thermochemical treatments.

branches of the hysteresis loop may be identified by exponential laws given by:

$$M^{\pm} = M_s [1 - e^{-\lambda(H \pm H_c)}],$$

where $M^{\pm}$ represents the branch with increasing (decreasing) M , $H \geq H_c$ ($-H_c$), M_s is the saturation magnetization, and λ may be calculated from the measured H_c , M_s and M_r values, using the expression:

$$\lambda = H_c^{-1} \ln \left[\frac{M_s}{M_s - M_r} \right], \text{ since for } H = 0: M^- = M_r.$$

Thus, the λ values of the NTT and CTT samples ($\text{Co}_{74}\text{Fe}_8\text{B}_{12}\text{Si}_6$) were 12 and 15×10^{-3} , respectively. For the nitrided sample containing 4% at. Mn, λ value was 11×10^{-3} . Furthermore, the shape of the hysteresis loops for the CTT samples appears to be different from the NTT samples. Some authors (Srivastava and Vishwamittar 1988) use the parameter λ , as an indicator of the degree of softness of the material.

Figure 5. The curves fitted by the exponential law follow the same trend as the hysteresis loops obtained by VSM.

The curves fitted by the exponential law are presented in figure 5. The curves show the same trend as the hysteresis loops obtained by VSM. However, for the sample containing manganese, the fit is not nearly as comparable.

4. Conclusion

We have shown that the nitriding thermochemical treatment, commonly used for steels, is technically feasible in the case of ribbons as well, and show nitrogen diffusion throughout the sample. Furthermore, the coercive field was lower in the case of NTT ribbons compared to CTT ribbons. It should be noted however that with such treatments the comparison is possible only with crystallized samples.

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