Anisotropic thermal expansion of as-cast RQM ribbons and magnetic anisotropy

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Abstract. Less expansion and more shrinkage along the ribbon axis than transverse to the axis is generally observed during temperature cycle when the dilatation of as-cast ribbons is measured. This anisotropy is seen to relax together with modest as-cast magnetic anisotropy if the sample has been cycled up to ~400°C prior to the test. Often but not always, the as-cast magnetic anisotropy shows the sign as expected after tensile stress annealing. During ribbon solidification, tensile stress can create anelastic strain or even structural anisotropy which results in both the observed anisotropies. Ribbons quenched on air are known to bear some macroscopic heterogeneity which acts by forces between surfaces and ribbon interior. These forces could interfere with the relaxation of the as-cast anisotropies. Tests show that the interference is weak and the heterogeneity acts isotropic in the ribbon plane and induces magnetic anisotropy of its own.

1. Introduction

The term “Anisotropic Thermal Expansion” (ATE) is used in this work to indicate the following attributes observed at dilatation measurement (i.e. during annealing) along the ribbon length if compared to transverse direction: Identifiably smaller thermal expansion, more pronounced reduction of expansion or even transient shrinkage above ~200°C, significantly larger net shrinkage after ending the temperature cycle despite of the peak temperature (T > 350°C) used. This anisotropy is a feature of so called structural relaxation in the amorphous state and for the studied materials it decays fairly below the onset of crystallization as demonstrated by repeating the temperature cycle (e.g.[1]). This anisotropic behavior looks as if the ribbons solidified under a tensile stress and bear some resulting anelastic strain or even structural anisotropy [2]. Large majority of materials studied so far in our laboratory show at least modest magnetic anisotropy of hard-ribbon-axis (HRA) type in the as-cast state. Again, the most materials showing HRA as-cast anisotropy belong to the class of composition, where tensile-stress annealing results in just this type of magnetic anisotropy [3]. To see this correlation as causal is tempting even if one does not forget that, unlike the rapid quenching, the stress annealing is a solid state process. Moreover, there is another effect capable of interfering with the relaxation of anelastic strain or structural anisotropy. Ribbons quenched on air are known to bear some macroscopic heterogeneity (MH) which acts by forces between surfaces and ribbon interior [4].
The forces may not be disabled at the relaxation. In this work we attempt to shed more light on the correlation of ATE and as-cast magnetic anisotropy as well as on the possible influence of MH.

### 2. Experimental

FeNbCuBSi Finemets and low-magnetostrictive CoCrFeBSi metallic glass (for comparison) is studied. All the ribbons of various widths (10 to 40 mm) are prepared by planar-flow casting of the melt on air. Particular composition of the wider (20÷40 mm) ribbons is quoted in the Table. The rectangular samples’ longer sides are cut along (L) and transverse (T) to the ribbon long axis. Tensile dilatometry uses a capacitive sensor and is performed in Ar or air. Magnetic measurement in Helmholtz coils only uses the wider ribbons to enable similar dimensions of L and T samples and not to surpass 4E-4 for the demagnetization factor. A digitizing hysteresisgraph records the loops at sinusoidal 21 Hz excitation. The evaluation of anisotropy KT-L (see Fig. 2) gives an error of ±2 J/m³.

### 3. Results and Discussion

| Material                  | as-cast | 400°C vacuum | 400°C Ar | 540°C vacuum | 540°C Ar |
|---------------------------|---------|--------------|----------|--------------|----------|
| Fe74.5Nb3Cu1B15Si6.5     | -100    | ~0           | <0       | -26          | -4       |
| Fe73.4Nb3Cu1B13Si3.6     | -189    | +32          | ~0       | ~0           | ~0       |
| Fe73.3Nb3Cu1B15Si15.5    | -225    | >0           | -20      | -11          | -10      |
| Co67Cr7Fe4B14Si8         | -14     | ~0           | <0       | -            | -        |

Compositionally different Finemets show quantitatively different dilatation behavior (Fig.1). The net shrinkage is in good agreement with the observed density changes [5]. Nevertheless, both the materials show the ATE attributes if longitudinally cut samples (L) are compared to the transversally cut ones (T). ATE seems to be an universal property which does not reflect magnetostriction or Invar effect or surface quality because these properties differ qualitatively among the ribbons tested unlike ATE. ATE does not vary systematically with ribbon width at least in the 10÷40 mm range. MH could be a suspect source of ATE since MH produces squeezing surfaces on Finemets containing less than 13 at.% Si [4]. At least the anisotropic net shrinkage is not principally caused by MH because the shrinkage shows almost the same anisotropy of dimensional changes if vacuum annealed samples are compared to Ar-annealed ones whereas MH is known to create far stronger squeeze during annealing in Ar than in vacuum. Nevertheless, minor differences of dilatation behavior in Ar and air can be observed above ~350°C (where as-cast MH starts to transform [5]).

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**Figure 1.** Dilatation of 10 mm wide ribbons. L, T denote sample length (principal measurement direction) oriented along and across the ribbon axis respectively.
Example of the as-cast magnetic anisotropy is given by Fig. 2. The transversally cut sample (T) shows easier magnetization than the longitudinally cut one (L). This is what is called HRA anisotropy in this work. It is characterized by a negative value of magnetization work difference (shaded area). The opposite would be ERA – easy ribbon axis anisotropy with a positive KT-L. The samples bear almost equal geometric demagnetization factors (the loops are correspondingly corrected; \( H_i \) denotes internal field). It appears, the larger net shrinkage (see dilatation inset), the larger magnetization work. One would expect similar result when this (solid) material were annealed under tensile stress along the ribbon axis. This HRA type is by far the most observed (though not exclusively) as–cast magnetic anisotropy.

The anisotropic dimensional change featuring preferred longitudinal shrinkage is observed also when the \( \lambda \sim 0 \) Co metallic glass is annealed (Fig. 3). Similarly to the FeNbCuBSi Finemets, tensile stress annealing of this metallic glass produces the HRA-type magnetic anisotropy [6]. However different ribbons (composition and 25 mm width are the same) show different types of weak as-cast magnetic anisotropy – the upper loops show ERA whereas the lower loops display HRA. Very weak HRA anisotropy is also universally observed after 400°C relaxation in Ar (Table). Thus the HRA anisotropy could be promoted by a partial relaxation of the as-cast ribbon. The ribbon showing HRA is thicker and has been cast from a colder melt. The other ribbon (thinner by 20 %) shows minor ERA anisotropy which reverts to very weak HRA anisotropy only after Ar annealing. The thicker ribbon shows smaller relaxation enthalpy at a calorimetric check (DSC). It means that its quenching rate was lower and/or it was already partially relaxed if compared to the thinner ribbon. 40 mm wide ribbons of this metallic glass showed another pattern. Although its dilatation displays ATE as well, the as-cast magnetic anisotropy is evidently ruled by transversal heterogeneity – the resulting as-cast anisotropy depends on where the L sample was cut from. If a L sample from the center is compared to a T sample, weak ERA anisotropy is the result. Using near-edge L sample gives HRA. The different ribbons show that there is no straightforward general correlation of as-cast magnetic anisotropy to the universally observed ATE or mere anisotropic shrinkage. One can hypothesize that the as-cast strain supports a structural variation (structural anisotropy) as in the case of homogeneously deformed metallic glasses [7].
structural variations can be diverse in the different ribbons because certain essential parameters (e.g. quenching rate) were different during casting of these ribbons.

The action of the macroscopic heterogeneity (MH) is shown in Fig. 4. Due to MH, surfaces squeeze (in-plane compression $\sigma_{\text{MH}}$) the ribbon interior and tilt the loop of a positively magnetostrictive material driving the easy direction off the ribbon plane via the magnetoelastic interaction $\sim \lambda \times \sigma_{\text{MH}}$. This material is the most magnetostrictive of all the wide ribbons studied (after 540°C Ar anneal $\lambda_s \sim +6\times10^{-6}$) and its loops are seen much more tilted after Ar anneal than after vacuum anneal – a benchmark of MH. Somewhat surprisingly, the action of MH is fairly isotropic as it tilts the L-T loop pairs “coherently”. This is the only type of behavior observed so far on various Finemet ribbons and compositions. This isotropy does not seem to be significantly influenced by different surface quality or ribbon width or thickness. As for the correlation ATE – MH, a weak hampering of as-cast magnetic anisotropy decay is seen best on Si-rich Finemets (-20 J/m² in the Table), where the MH surface-squeeze is at its weakest or it has possibly reverted to spreading. Altogether, the magnetic response of the ATE – MH interaction is a weak one.

4. Conclusions

- The anisotropy of thermal expansion appears to be a rather universal property of rapidly quenched amorphous metallic ribbons.
- A sort of structural anisotropy, probably based on the bond-orientational anisotropy [2], is capable of explaining the origin of the observed HRA-type as-cast magnetic anisotropy. However, the occurrence of ATE merely indicates an anelastic strain which often goes together with an induced structural anisotropy [7].
- The macroscopic heterogeneity shows fairly isotropic magnetoelastic action so that the product $\sigma_{\text{MH}} \times \lambda$ could be regarded isotropic. MH is not the principal source of ATE although it can slightly hamper the relaxation of ATE.

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Figure 4. Influence of macroscopic heterogeneity.