MAGNETIC AND SURFACE PROPERTIES OF FE-NB (MO, V)-CU-B-SI RIBBONS

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1. Introduction

The rapidly quenched Finemet (FeNbCuBSi) ribbons prepared by planar flow casting of the melt are very variable to obtain very good soft-magnetic properties. An appropriate thermal treatment leading to ultra-fine grain structure enables to attain such properties as desired for practical use [1]. Increasing Fe percentage to the detriment of non-magnetic components lifts saturation induction above 1.3 T [2], preserves low coercivity and makes the alloy even cheaper to suit its mass production for use in power electronics. Apart from the plenty of benefits the ribbons show some risks. One of them is macroscopic heterogeneity, which often manifests via differences between surfaces and interior of a ribbon [3]. The surfaces squeeze (by in-plane force) the interior of many such ribbons and if engaged in magnetoelastic interaction, the force affects the resulting magnetic anisotropy [4]. Current research shows that changes of hysteresis loop shape come rather from surface crystallization and not from oxides namely in positively magnetostrictive alloys FeNbCuBSi known as low-Si Finemets [5]. The object of this work is to verify whether the substitution of another element instead of Nb (usually incorporated as the grain-growth blocker) can change surface properties and affects the resulting magnetic properties. We chose V and Mo instead of Nb. Oxides, oxy-hydroxides and a possible squeezing layer was looked for after higher temperature annealing which ensures partially nanocrystalline structure.

2. Experimental Details

The ribbons of Finemet type $Fe_{77}(M)_3Cu_1B_{14}Si_5$ where M = Nb, Mo and V, were prepared by planar-flow casting in air. As-cast samples with a thickness of 21 μm were cut to strips with 10 cm length and 6 mm width. Sufficiently nanocrystalline state was obtained by annealing at 520°C for 1 hour in Ar atmosphere. Thermogravimetry and differential scanning calorimetry were performed by STA Q600 analyzer at 10°C/min rate. For investigation of structure and crystalline phases, X-ray diffraction (RD) was used. The investigated ribbons are positively magnetostrictive with coefficient of saturation magnetostriction λ_s about 10^{-5} after annealing. Hysteresis loops were recorded using a digitizing hysteresisgraph at standard ac (21 Hz) sinusoidal *H* excitation in Helmholtz drive coils. To investigate the surface chemistry of the ribbons, they were observed by Raman spectroscopy (RS) using confocal system with 632.8 nm radiation from He-Ne laser with the back-scattering geometry.

3. Results and Discussion

As-cast ribbons were investigated by thermal analysis in Ar atmosphere to find out critical temperatures. Whereas “Nb” and “Mo” ribbons show alike shape of variations and only small difference of Curie temperature (T_C), ribbon “V” shows higher T_C by almost 70°C, although the corresponding crystallization temperatures of “V” are not so much higher (Table

1.), Vanadium, being a smaller 3d atom/ion than 4d Nb or Mo works differently – it shows good miscibility with Fe to form a solid solution and, lacking segregation tendency, V does not promote formation of Fe clusters, which become the nuclei of bcc Fe crystals during annealing. Vanadium does not tamper with the spin-split valence band of Finemet alloy so much as the electron-richer 4d metals do [6].

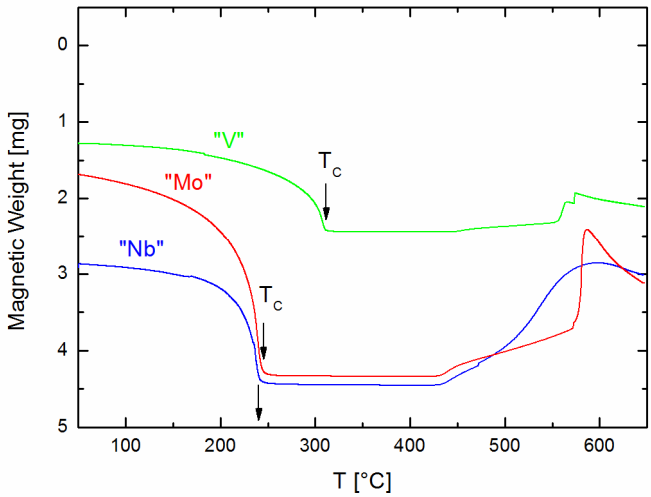


Fig.1: *Thermo-gravimetric curves of $Fe(M)_3CuBSi$ for M = Nb, V and Mo ribbons.*

Temperatures of crystallization onset (T_x) and of the first crystallization maximum (T_p) were measured simultaneously with thermo-gravimetric curves.

Tab. 1. *Critical temperatures of metallic ribbons measured by STA at 10 °C/min rate.*

Alloy	**T_C** [°C]	**T_x** [°C]	**T_p** [°C]
$Fe_{77}Nb_3Cu_1B_{14}Si_5$	240	434	446
$Fe_{77}Mo_3Cu_1B_{14}Si_5$	243	433	445
$Fe_{77}V_3Cu_1B_{14}Si_5$	310	450	461

To gain sufficient and comparable crystalline share to enable investigation of suspect force action of surfaces on the magnetic properties (hysteresis loops), we chose higher annealing temperature (520°C). Hysteresis loops of the annealed ribbons are shown in Fig. 2a. The substitution of Mo for Nb resulted in very similar shape of loop with a central belly and slant part at medium field H. This loop shape is typical for a significant hard-ribbon-axis anisotropy component that comes from macroscopic forces where surfaces compress the ribbon interior. Another effect is seen for sample “V”, its loop is wider and has round shape. Its coercivity had notably risen what is assumed to be caused by the growth of grains and also the appearance of Fe boride (magnetically harder) in the partially crystallized sample.

XRD patterns are shown in Fig. 2b where the spectrum shows discernible tetragonal Fe_2B phase peaks (not marked) for “V” sample only. The diamond-marked peaks correspond to the “standard” bcc Fe(Si) phase. The approximate grain size was calculated using Scherrer formula. It differs markedly for the three – “Nb, Mo, V” compositions: 14±2 nm, 27±2 nm, 32±5 nm respectively. The grain size is obviously reflected in coercivity [2] as seen in Fig. 2a

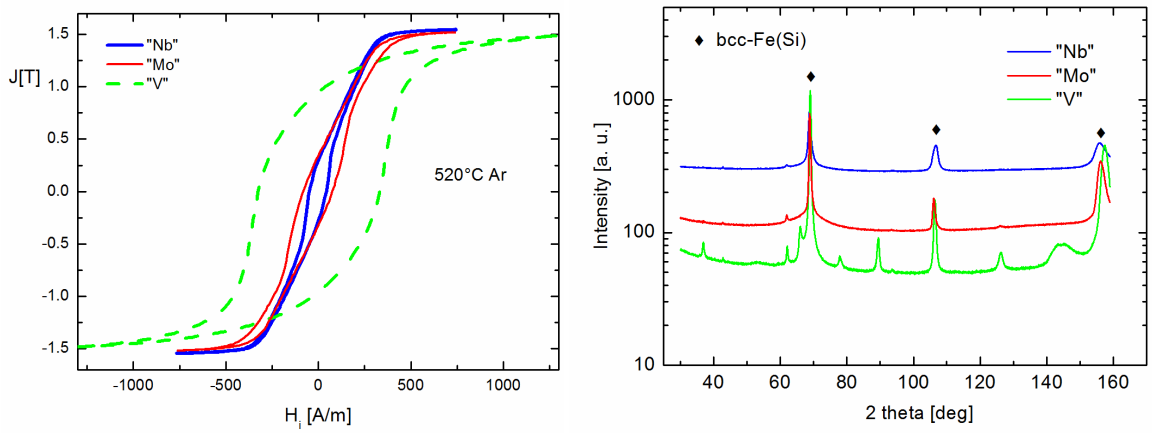
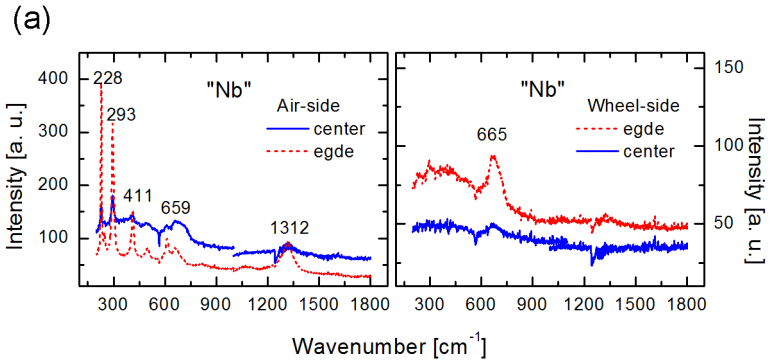


Fig. 2: *Left – a) Hysteresis loops of annealed $Fe(M)_3Cu$ BSi for M = Nb, Mo and V ribbons as labelled; right – b) XRD pattern for the same ribbons annealed at 520°C in Ar.*

whereas an additional coercivity for “V” sample can come from the boride too.

The loop tilt of “Nb” and “Mo” samples notably increased by annealing in Ar if compared to equivalent vacuum annealing, where the loops (not shown) are quite upright and slim. This convincingly points to some compressing/squeezing exerted on the major volume (interior) of the positively magnetostrictive ribbons. Due to the large coercivity and poor approach to saturation seen on the “V” loop, a likely loop tilt is hardly discernible. It is thus quite possible that there is no significant squeeze of surfaces on ribbon interior to be reflected by magnetic response of the V-containing alloy. Though, the coercivity after Ar-annealing is larger than after 520°C vacuum annealing but it is matched by annealing at higher temperature (540°C). This progression suggests that Ar annealing causes somewhat more advanced crystallization than vacuum annealing for this material too. Generally, all the three ribbons are suspect of preferred surface crystallization during Ar-annealing like we see in many similar materials [5]. There is another candidate potentially capable of exerting surface stress after Ar-annealing – the oxides or other compounds created in/on the surfaces.

Two remarkable features are noted at the first look (Fig. 3) on the Raman spectra: 1) iron oxides (Fe_2O_3&FeO) are the only oxides resolved well by RS, 2) pronounced peaks (i.e. RS selection rules followed well) are observed best at the ribbon edges. Apart from wheel-side edge, the "V" ribbon displays the least pronounced peaks but shows, probably adventitious, graphitic carbon (at ~1350, 1600 cm-1) as the only composition. None of the observed surface contaminants appear to form a contiguous layer as tested by SEM and optical microscopy - clear spectra were observed only if a contrasting tiny spot was targeted by laser beam. Thus RS confirms the appearance of certain surface oxides but provides no support for notion that the surface squeeze comes from the oxides.



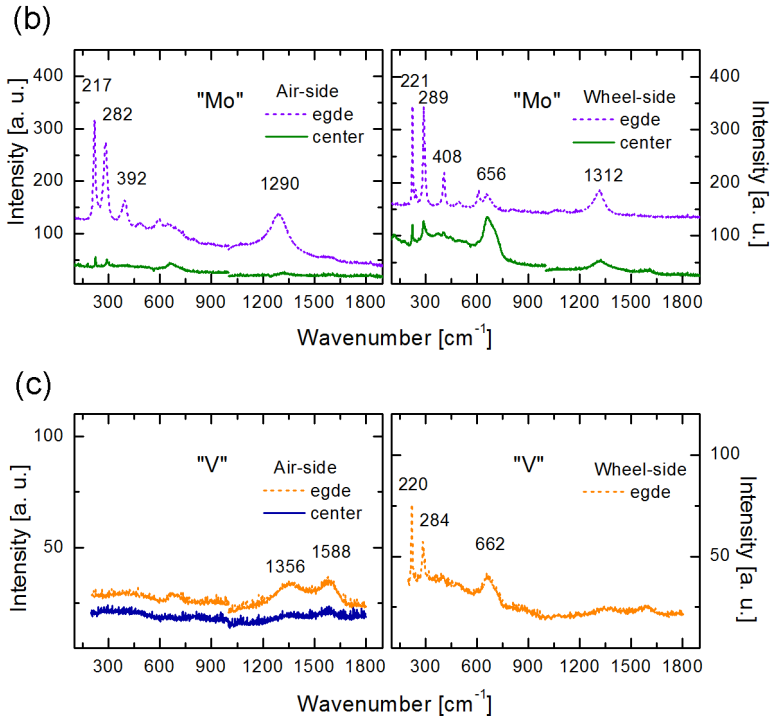


Fig. 3: *Raman spectra of $Fe(M)_3CuBSi$ for M = Nb, Mo and V ribbons annealed at 520°C/Ar.*

4. Conclusion

As this work is a first-stage investigation of Si-poor Finemet-based, substituted alloy set, only few questions are answered, other are opened. The macroscopic forces between surfaces and ribbon interior are active in Nb- and Mo-substituted ribbons for sure, for V-substituted ribbon possibly. To block grain growth, Nb is the best element followed by Mo, V appears to be the least efficient. The following remain to be investigated in more depth: Crystallization appears to start from ribbon surfaces, it is accompanied by surface oxidation during Ar annealing. It is still unclear whether there is causation between surface oxidation and crystallization, which from the two is the primary source of macroscopic forces and whether grain-growth blocking promotes the surface-interior difference (heterogeneity).

Acknowledgement

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