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Effects of high temperature treatments in air and argon on the magnetic properties of HITPERM alloys

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Abstract

The oxidation behavior of the HITPERM alloy series $Fe_{60}Co_{18}Nb_{6-x}Zr_xB_{16-z}Cu_z$ (x = 0, 3, 6; z = 0, 1) was studied. After heating up to 1073 K, an oxide layer ~1 μm thick with a two-layer structure (the outer enriched in Fe) can be identified previous to a sharp interface between the oxide layer and the alloy matrix, where no oxygen is detected. The alloys with Zr oxidize faster than the alloys without Zr. Magnetic properties of nanocrystalline samples annealed 20 h at 673 K in air and argon show no change. However, after 50 h at 773 K, the coercivity of the samples increases, the effect being more significant for the alloys without Zr than for those with Zr, independently of the gas environment during the annealing. No change was observed in the microstructure after annealing and, therefore, the magnetic hardening must be due to some changes in the residual amorphous matrix.

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Keywords: HITPERM; Nanocrystalline alloys; Oxidation; Coercivity

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Soft magnetic nanocrystalline alloys, in which crystallites of about 10 nm are embedded in a residual amorphous matrix, have been developed as excellent candidates for soft magnetic applications [1]. This microstructure, which yields an averaging out of the magnetocrystalline anisotropy [2], is responsible for the outstanding magnetic properties observed. At the end of the last decade, new compositions FeCoMBCu, the so-called HITPERM alloys [3], extended the applicability of nanocrystalline alloys up to higher temperatures, due to the increase of the Curie temperature of the residual amorphous phase. Although Cu addition is known to reduce the grain size in FINEMET and NANOPERM alloys through Cu-clustering [1], Cu clusters do not form in Zr-containing HITPERM alloys [4]. However, Cu-clustering occurs and refines the microstructure of Nb-containing HITPERM alloys [5]. To check the real possibilities for high temperature technological applications of these materials the study of the compositional effects on the nanostructure stability [6] and the oxidation behavior of HITPERM–type alloys are key questions.

In this work, the oxidation behavior in air and the effect of high temperature treatments in air and argon atmospheres on the microstructure stability of nanocrystalline $Fe_{60}Co_{18}Nb_{6-x}Zr_xB_{16-z}Cu_z$ (x = 0, 3, 6; z = 0, 1) melt-spun ribbons (~ 5 mm wide and ~ 15-40 μm thick) were studied. In the following the compositions will be denoted as *Nb0* (x=0, z=0), *Nb1* (x=0, z=1), *NbZr1* (x=3, z=1) and *Zr1* (x=6, z=1). The oxidation process was studied using a thermobalance (TG) Perkin-Elmer TGA7, in order to obtain the in-situ mass gain of the samples during the heat treatments. Scanning electron microscopy (SEM)

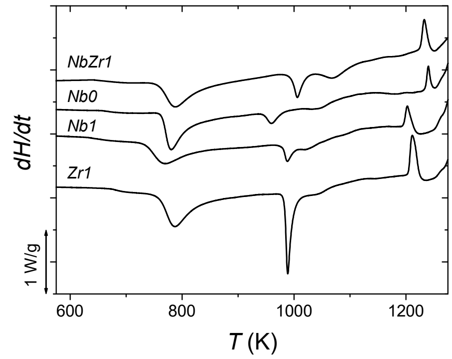

Fig. 1. DSC scans at 20 K/min of the as-cast studied alloys.

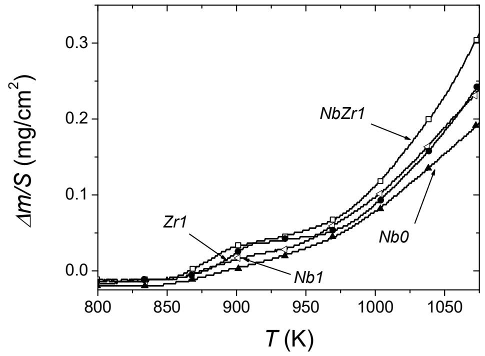

Fig.2. Specific mass gain obtained at 40 K/min by TG for the studied alloys

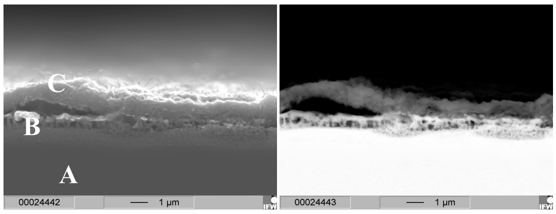

Fig. 3. SEM images showing the structure of the oxide layer of *NbZr1* alloy heated up to 1073 K. Left, SE image; right, BSE image. The labels A, B, C correspond to the alloy matrix, the inner oxide layer and the outer oxide layer, respectively.

images from back scattered electrons (BSE) and secondary electrons (SE) were used to study the formed oxide layer and its composition was obtained by energy dispersive X-ray spectroscopy (EDX). A Netzsch DSC 404 differential scanning calorimeter (DSC) was used to study the devitrification process (in argon atmosphere) and the long time annealing of samples in air and argon atmospheres. The microstructure (lattice parameter, *a*, grain size, *D*, and crystalline volume fraction, *X*) was studied using a Philips PW 1050 diffractometer with Co Kα radiation. Coercivity, H_C, was measured using a Förster Koerzimat. Figure 1 shows DSC scans at 20 K/min for as-cast samples of the four studied alloys. Two main exothermic peaks are detected: the first one (~750 K) corresponds to the formation of α-Fe type nanocrystals and the second one (~1000 K) to the formation of boride phases [7]. The endotherm observed above 1200 K corresponds to the α-γ transition of Fe.

Figure 2 shows the mass gain of the as-cast alloys as a function of the temperature. Below 850 K there is no significant mass change but at this temperature an increase occurs (faster for Zr-containing alloys), which saturates at about 0.05 mg/cm^2 of mass gain. Above 975 K a new mass increase is observed, which does not saturate in the temperature range of our experiment. After this treatment (heating in air up to 1073 K) the microstructure of the samples was studied by XRD, SEM and EDX. In agreement with DSC results, XRD shows that samples are fully crystallized and, besides α-Fe and borides, Fe_3O_4 and Fe_2O_3 lines appear. SEM pictures (an example is shown in Fig. 3 for *NbZr1* alloy) show a clear interface between the alloy matrix (without contrast by SE) and the oxide layer (showing porosity by SE). The oxide layer is ~1 μm thick and shows a two-layer structure (clearly observed by BSE). The outer oxide layer is richer in O and Fe and the inner one is enriched in Co, Zr and/or Nb. The alloy matrix is oxygen free and the ratio between Fe, Co, Zr and Nb is that of the nominal composition. B content can not be measured with this technique.

Nanocrystalline samples (*X*~70-80 %, and *D*~8-15 nm) of the different alloys were obtained after annealing the corresponding amorphous precursor alloys during 5 min at 873 K in argon. Then, they were submitted to an additional long time annealing in air or argon atmosphere in order to study the compositional dependence of the oxidation and the thermal stability of the microstructure as well as their effects on the magnetic properties. TG results on samples annealed 50 h at 773 K show a mass gain lower than 0.05 mg/cm^2 for the alloys with Zr (which would correspond to an oxide layer ~100 nm thick) and a negligible increase for the Zr-free alloys (<0.015 mg/cm^2). The long time annealing do not apparently modify the microstructure of the nanocrystalline samples observed by XRD (see table I) and *a* and *D* values remain constant.

No appreciable change can be observed for the magnetic properties of nanocrystalline samples after annealing 20 h at 673 K in air or argon with respect to the non-additionally annealed nanocrystalline samples. However, annealing for 50 h at 773 K in air yields a clear magnetic hardening for all the studied compositions, being higher for the Zr-free alloys, which is opposite to the expected effect if the formation of oxides were the responsible for this magnetic hardening. In order to understand this fact, the annealing was repeated in argon for *Nb1* and *Zr1* alloys and no significant change was observed with respect to the air-annealed samples (see table II). Consequently, this hardening can not be due to the oxide formation. On the other hand, the nanocrystals show no changes after the annealing (nor compositional, through a change of *a*, neither grain coarsening) and there are no traces of boride phases in the XRD patterns. Therefore, the magnetic hardening of the alloys observed after 50 h at 773 K must be due to some change in the residual amorphous matrix, implying different environments for Nb and Zr atoms, which could be associated to the different crystalline phases formed during the second crystallization stage. In fact, Zr-free alloys show a clear increase in M_S after annealing at 773 K in air with respect to non-additionally annealed nanocrystalline samples. However, the increase observed after annealing 773 K in argon is at the limit of the error bar (see table I). Heat treatments in air or hydrogen could yield a migration of B to the surface where it is removed from the alloy as oxide or hydride [8, 9], which would modify the amorphous composition and would even facilitate an increase of the α-Fe phase. This phenomenon seems to be less effective in Zr containing alloys.

In conclusion, nor oxidation neither grain coarsening are relevant to describe the magnetic hardening observed in nanocrystalline HITPERM-type studied alloys after long time annealing at 773 K. This coercivity increase, higher in the alloys without Zr, might be associated to changes in the residual amorphous matrix involving the Zr or Nb atomic enviroments.

Table I. Microstructure and magnetic properties of nanocrystalline alloys without additional annealing treatment (Nano) and after two additional long time annealing: 20 h at 673 K and 50 h at 773 K.

alloy	Nano 5 min 873 K	+ 20 h 673K		+ 50 h 773 K	
		Argon	Air	Argon	Air
Nanocrystal grain size ($D \pm 2$) nm					
Nb1	8	8	8	9	9
Nb0	15	15	15		15
NbZr1	8	8	8		8
Zr1	9	8	8	15	12
Lattice parameter of α-Fe,Co ($a \pm 0.005$) 10^{-10} m					
Nb1	2.867	2.865	2.866	2.864	2.863
Nb0	2.871	2.868	2.868		2.868
NbZr1	2.869	2.868	2.863		2.865
Zr1	2.870	2.869	2.869	2.869	2.869
Coercivity ($H_C \pm 5$ A/m)					
Nb1	26	32	33	133	137
Nb0	43	57	55		222
NbZr1	22	26	28		89
Zr1	29	26	29	96	83
Saturation Magnetization ($M_S \pm 5$ emu/g)					
Nb1	165	161	164	177	196
Nb0	180	176	179		205
NbZr1	165	161	163		163
Zr1	174	176	167	165	174

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References

[1] M.E. McHenry, M.A. Willard, D.E. Laughlin, Progress in Mater. Sci. 44 (1999) 291.

[2] A. Hernando, M. Vázquez, T. Kulik, C. Prados, Phys. Rev. B 51 (1995) 3581.

[3] M.A. Willard, D.E. Laughlin, M.E. McHenry, D. Thoma, K. Sickafus, J. O. Cross, V. G. Harris, J. Appl. Phys. 84 (1998) 6773.

[4] D.H. Ping, Y.Q. Wu, K. Hono, M.A. Willard, M.E. McHenry, D.E. Laughlin, Scripta Mater. 45 (2001) 781.

[5] Y. Zhang, J.S. Blázquez, A. Conde, P.J. Warren, A. Cerezo, Mat. Sci. Eng. A 353 (2003) 158.

[6] J. Ferenc, J. Latuch, T. Kulik, J. Magn. Magn. Mater. 272-276 (2004) 1469.

[7] J. S. Blázquez, C. F. Conde, A. Conde, J. Non-Cryst. Solids 287 (2001) 187.

[8] G. Wei, B. Cantor, Acta Met. 36 (1988) 2293.

[9] G. Saage, S. Roth, J. Eckert, L. Schultz, Mat. Sci. Eng. A 375-377 (2004), 1125.