

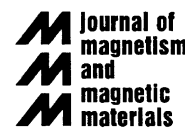


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# Effects of high temperature treatments in air and argon on the magnetic properties of HITPERM alloys

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## Abstract

The oxidation behavior of FeCo(NbZr)B(Cu) alloy series was studied. After heating up to 1073 K, an oxide layer  $\sim 1 \mu\text{m}$  thick with a two-layer structure can be identified previous to a sharp interface between the oxide layer and alloy matrix, where no oxygen is detected. The coercivity of nanocrystallized samples increases, independently of the gas environment, during additional long-time-annealing without a significant change of the microstructure.

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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 HITPERM alloys (FeCoMBCu) [3] extended the applicability of nanocrystalline alloys up to higher temperatures, due to an increase of the Curie temperature of the residual amorphous phase. To check the real possibilities for the high temperature technological applications of these materials, the study of compositional effects on the nanostructure stability [4] and the oxidation behavior of HITPERM-type alloys are the 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  $\text{Fe}_{60}\text{Co}_{18}\text{Nb}_{6-x}\text{Zr}_x\text{B}_{16-z}\text{Cu}_z$  ( $x = 0, 3, 6; z = 0, 1$ ) melt spun ribbons ( $\sim 5 \text{ mm}$  wide and  $\sim 15\text{--}40 \mu\text{m}$  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, to obtain in situ mass gain of the samples during the heat treatments. Scanning electron microscopy (SEM) 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  $\text{Co K}\alpha$  radiation. Coercivity,  $H_C$ , was measured using a Förster Koerzimat. Saturation magnetization,  $M_S$ , was measured in a vibrating sample magnetometer (VSM). Fig. 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 ( $\sim 750 \text{ K}$ ) corresponds to the formation of  $\alpha$ -Fe-type nanocrystals and the second one ( $\sim 1000 \text{ K}$ ) to the formation of boride phases [5]. The endotherm observed above 1200 K corresponds to the  $\alpha$ - $\gamma$  transition of Fe.

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Fig. 2 shows the mass gain of the as-cast alloys as a function of temperature. Below 850 K there is no significant mass change but at this temperature an increase occurs (faster for Zr-containing alloys). Above 950 K, the mass gain increases faster. After this treatment (heating in

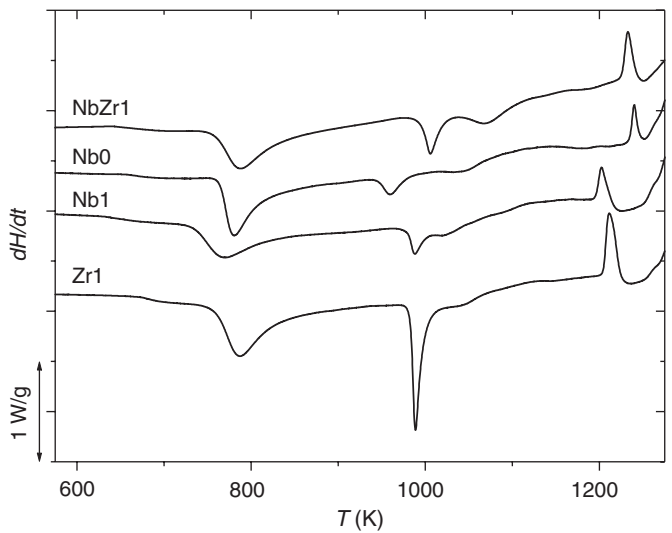


Fig. 1. DSC scans at 20 K/min of the as-cast studied alloys.

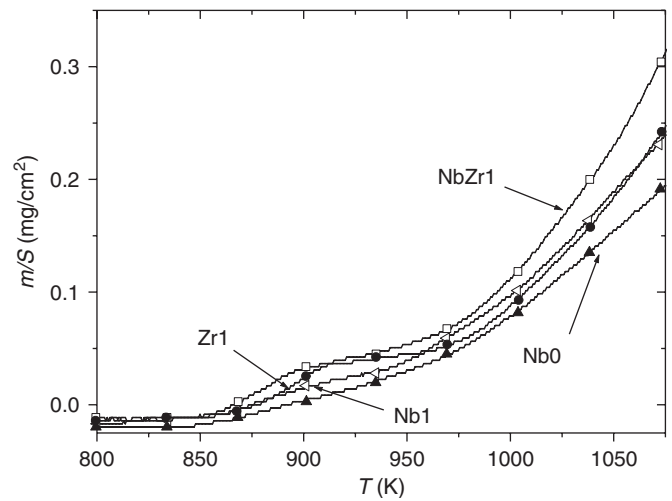


Fig. 2. Specific mass gain obtained at 40 K/min by TG for the studied alloys.

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  $\alpha$ -Fe and borides,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  lines appear. The 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 about 1  $\mu\text{m}$  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 could not be measured.

Nanocrystalline samples ( $X \sim 70\text{--}80\%$ , and  $D \sim 8\text{--}15\text{ nm}$ ) of different alloys were obtained after annealing the corresponding amorphous precursor alloys during 5 min at 873 K in argon. Then, these samples were submitted to an additional long time annealing in air or argon atmosphere to study the compositional dependence of the oxidation and the thermal stability of the microstructure as well as their effects on the magnetic properties (Table 1).

Table 1  
Physical properties of nanocrystalline samples

Alloy		5 min 873 K	+20 h/673 K argon/air	+50 h/773 K argon/air
Nb1		8	8/8	9/9
Nb0	$D \pm 2$	15	15/15	—/15
NbZr1	(nm)	8	8/8	—/8
Zr1		9	8/8	15/12
Nb1		2.867	2.865/2.866	2.864/2.863
Nb0	$a \pm 0.005$	2.871	2.868/2.868	—/2.868
NbZr1	( $10^{-10}\text{ m}$ )	2.869	2.868/2.863	—/2.865
Zr1		2.870	2.869/2.869	2.869/2.869
Nb1		26	32/33	133/137
Nb0	$H_C \pm 5$	43	57/55	—/222
NbZr1	(A/m)	22	26/28	—/89
Zr1		29	26/29	96/83
Nb1		165	161/164	177/196
Nb0	$M_S \pm 10$	180	176/179	—/205
NbZr1	(emu/g)	165	161/163	—/163
Zr1		174	176/167	165/174

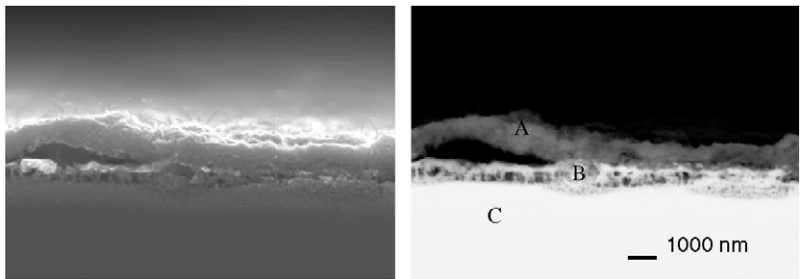


Fig. 3. SEM images of NbZr1 alloy heated up to 1073 K. Left, SE image; right, BSE image. (A) Outer oxide layer; (B) inner oxide layer; and (C) alloy matrix.

TG results on nanocrystalline samples additionally annealed 50 h at 773 K show a mass gain lower than  $0.05 \text{ mg/cm}^2$  for the alloys with Zr (corresponding to an oxide layer  $\sim 100 \text{ nm}$  thick) and a negligible increase for the Zr-free alloys ( $< 0.015 \text{ mg/cm}^2$ ). Long time annealing does not apparently modify the microstructure of the nanocrystalline samples observed by XRD ( $a$  and  $D$  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. To understand this fact, Nb1 and Zr1 nanocrystalline samples were annealed in Ar (50 h at 773 K) and no significant change was observed with respect to the air-annealed samples. Consequently, this hardening cannot be ascribed to the oxide formation. As nanocrystals show no changes after this second annealing, 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 associated with the different crystalline phases formed during the second crystallization stage. A small amount of these phases, undetectable by XRD, could be formed acting as the domain pinning centers, as it was shown for FINEMET alloys [6]. 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 at 773 K in argon is at the limit of the error bar. The heat treatments in air or hydrogen could yield a migration of B to the surface where it was removed from the alloy as oxide or hydride [7,8],

which would modify the amorphous composition and would even facilitate an increase of the  $\alpha$ -Fe phase. This phenomenon seems to be less effective in Zr containing alloys.

In conclusion, neither the oxidation (the same effect is observed for samples annealed in air or argon) nor the 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 environments yielding an increase of magnetoelastic anisotropy or/and the possible formation of small amount of borides, which would act as pinning centers.

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