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## Magnetic permeability of $(\text{FeCoGe})_{88}\text{Zr}_6\text{B}_5\text{Cu}_1$ alloys: Thermal stability in a wide temperature range

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Temperature dependence, from room temperature up to 1000 K, of the initial permeability ( $\mu$ ) of  $\text{Fe}_{83-x}\text{Co}_x\text{Ge}_5\text{Zr}_6\text{B}_5\text{Cu}_1$  ( $x=5$  and 20) alloys at different stages of devitrification is reported. As nanocrystallization progresses, room temperature  $\mu$  decreases but high temperature one increases, leading to an improvement of its thermal stability extended from room temperature up to 915 K, characterized by a temperature coefficient of permeability  $\sim 0.1\%/K$  ( $\mu \sim 4000$ ) and  $0.04\%/K$  ( $\mu \sim 800$ ) for 5 and 20 at. % Co containing alloys, respectively. © 2008 American Institute of Physics. [DOI: 10.1063/1.2828719]

Research activity on soft magnetic nanocrystalline alloys is a current field of interest since the development of Finemet alloy ( $\text{Fe}_{73.5}\text{Si}_{13.5}\text{Nb}_3\text{B}_9\text{Cu}_1$ ).<sup>1</sup> The specific nanostructure exhibited by these alloys, consisting of small ferromagnetic nanocrystals ( $\alpha$ -Fe type phase,  $\sim 10$  nm in size) embedded in a residual amorphous matrix, also ferromagnetic but with a lower Curie temperature, is the responsible for their outstanding soft magnetic properties: the magnetocrystalline anisotropy is averaged out as the exchange correlation length exceeds the structural correlation one.<sup>2</sup> Both technological applicability and fundamental physics underlying in such systems support the interest devoted to this research field,<sup>3</sup> yielding the development of new families of nanocrystalline alloys: Nanoperm<sup>4</sup> and HiTPerm.<sup>5</sup> The latter was proposed in the aim of extending the soft magnetic character of nanocrystalline alloys to higher temperatures by partial substitution of Co for Fe. Recently, another way was suggested using small additions of Ge instead of Co.<sup>6</sup>

In this work, thermal dependence of the initial permeability  $\mu$  from room temperature up to 1000 K has been studied as a function of microstructure for two Ge and Co containing Nanoperm alloys.

Amorphous ribbons ( $\sim 5$  mm wide and  $30 \mu\text{m}$  thick) of  $\text{Fe}_{83-x}\text{Co}_x\text{Ge}_5\text{Zr}_6\text{B}_5\text{Cu}_1$  ( $x=5$  and 20) alloys were prepared by melt-spinning technique (in the following Co5 and Co20 alloys). Permeability measurements were performed on toroidal samples by an induction technique, at 6 kHz and an applied field small enough to assure the measurement of initial permeability ( $\sim 1$  A/m). Details on the experimental set up can be found elsewhere.<sup>7</sup> Transmission electron microscopy (TEM) experiments were performed in a JEOL 2000 FX operated at 200 kV. Differential scanning calorimetry (DSC) was performed in a Perkin-Elmer DSC7.

Figure 1 shows the permeability measurements obtained during heating, indicating for each curve the temperature up to which the sample was heated previously. The DSC signal of as-cast samples at a heating rate  $\beta=7.5$  K/min are superimposed on the corresponding panels of the figure. For amorphous samples, permeability exhibits a Hopkinson peak:  $\mu$  diverges at the Curie point  $T_C^{\text{am}}$  due to the faster decrease to zero of the magnetic anisotropy than that of the magnetization.<sup>8</sup> After the Hopkinson peak,  $\mu$  abruptly decreases but, for higher temperatures, a new rise in  $\mu$  can be

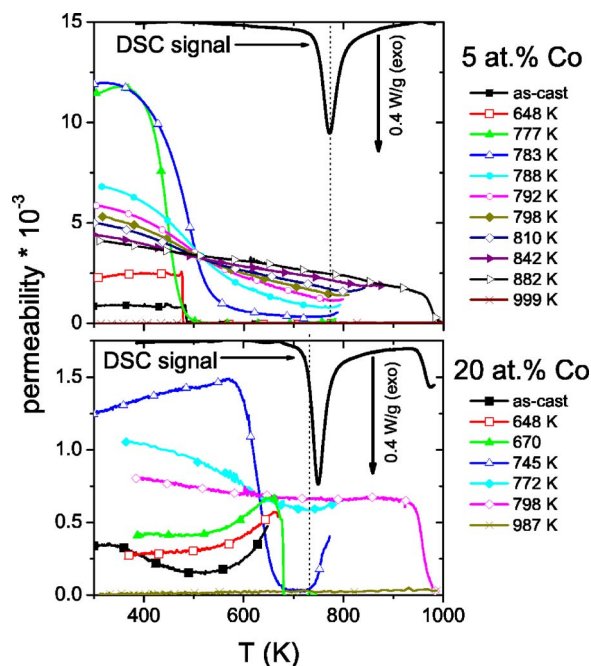


FIG. 1. (Color online) Thermal dependence of initial permeability for samples heated previously to different temperatures. Corresponding DSC plots are superimposed for comparison. The vertical dotted line indicates the crystallization onset temperature obtained from permeability measurements.

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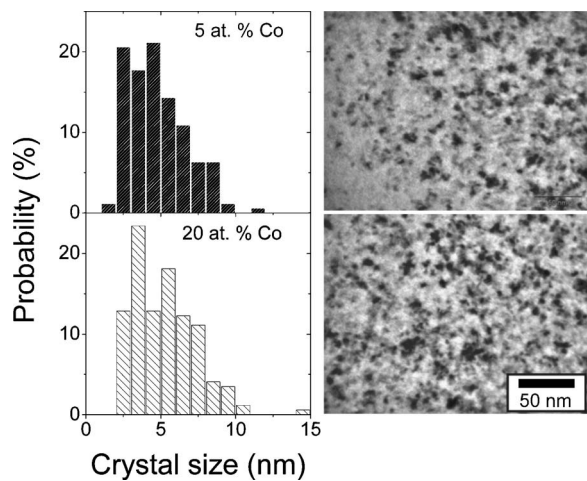


FIG. 2. TEM images and crystal size distribution for (upper) 5 and (lower) 20 at. % Co alloys heated up to 873 K.

observed corresponding to the onset of crystallization  $T_X$ . The crystallization onset temperatures detected at  $\beta = 7.5$  K/min in permeability experiments ( $T_X = 773$  and 731 K for Co5 and Co20, respectively) are higher than those measured by DSC ( $T_X = 747$  and 727 K for Co5 and Co20, respectively). Although magnetic measurements are generally claimed to be more sensitive to detect the crystallization onset of ferromagnetic particles emerging in a paramagnetic matrix<sup>9</sup> than calorimetric ones, the authors<sup>10</sup> have recently shown that, for a very fine nanocrystalline microstructure and small applied fields, this proposition can be untrue. The phenomenon was explained in terms of superparamagnetic behavior of uncoupled nanocrystals at the early stages of nano-crystallization.

TEM studies include crystallite size distribution for the two studied alloys, as shown in Fig. 2. It can be observed that crystal size extends up to 10 nm being the average grain sizes of 4.8 and  $5.3 \pm 0.5$  nm for Co5 and Co20, respectively. The explanation for the differences with the size reported in Ref. 11 is the formation of agglomerates of crystallites, crystallographically related as found for FeCoNbB (Ref. 10) and FeCoZrBCu (Ref. 12) alloys. These crystallographically related agglomerates will contribute as a single crystalline diffraction domain but detailed TEM images can evidence strong irregularities in the crystallite shape which could yield the identification of individual units with a more regular shape.

Fine nanocrystalline microstructure of the studied alloys and a rather low applied magnetic field ( $\sim 1$  A/m) explain the higher sensitivity of calorimetric techniques to detect the  $T_X$  than that of the magnetic method applied in this study. The smaller effect on the shift of onset temperature observed for Co20 alloy ( $\Delta T_X = 4$  K) than for Co5 alloy ( $\Delta T_X = 26$  K) cannot be ascribed to microstructural effects as, for both nanocrystalline alloys, are very similar (see Fig. 2). A possible explanation could be found in the smaller separation between  $T_C^{\text{am}}$  and  $T_X$  observed for Co20 than for Co5 alloy, which may lead to dipolar coupling among the crystallites.<sup>13</sup>

For samples heated above nanocrystallization onset, the Hopkinson peak is not detected, as there is no decrease to

zero in the magnetization at  $T_C^{\text{am}}$  ( $\alpha$ -Fe(CoGe) is ferromagnetic at this temperature). The value of  $T_C^{\text{am}}$  can be obtained from the intersection between the steepest slope tangent to the  $\mu(T)$  curve with the extrapolation to low temperatures of the  $\mu(T)$  curve from temperatures above the magnetic transition. Curie temperature decreases after relaxation ( $\Delta T_C^{\text{am}} \sim -13$  and  $-21$  K for Co5 and Co20, respectively), followed by an increase immediately after the nanocrystallization onset ( $\Delta T_C^{\text{am}} \sim 91$  and 7 K for Co5 and Co20, respectively). As nanocrystallization progresses,  $T_C^{\text{am}}$  increases with respect to the amorphous sample for Co5 alloy, whereas it decreases for Co20. This could be correlated with the different evolution of  $T_C^{\text{am}}$  for FeB and CoB amorphous alloys with the increase of B content.<sup>14</sup>

A strong increase in  $\mu$  values at room temperature is observed for samples heated just above the crystallization onset. Further increase of the crystalline volume fraction yields an increase of  $\mu$  at high temperatures and a decrease at low temperatures. It can be observed that soft magnetic properties are irreversibly lost above  $\sim 950$  K (see Fig. 1). This temperature corresponds to the second crystallization process detected by DSC (Ref. 11) yielding the formation of boride phases which magnetically harden the material.

The maximum room temperature  $\mu$  value is one order of magnitude larger for Co5 than for Co20 alloy. The microstructure, very similar for both systems, does not justify this difference between them (see Fig. 2). The average size of the nanocrystals,  $\sim 5$  nm, is small enough to ensure a good averaging out of the magnetocrystalline anisotropy of the ferromagnetic nanocrystals at temperatures where the amorphous matrix is still ferromagnetic.<sup>2</sup> The reason for this difference can be ascribed to other contribution to magnetic anisotropy: magnetoelastic anisotropy. In the case of Finemet alloys, besides the averaging out of magnetocrystalline anisotropy, outstanding soft magnetic properties are due to an almost zero magnetostriction.<sup>2</sup> This value results from a weighted average between the negative magnetostriction of the crystalline phase,  $\alpha$ -Fe(Si), and the positive one of the residual amorphous matrix. For the two studied alloys, neglecting the possible small amount of Ge inside the nanocrystals<sup>11</sup> and taking into account that no preferential partitioning of Co are observed in Fe based alloys,<sup>12,15</sup> the composition of the crystalline phase might be  $\text{Fe}_{100-x}\text{Co}_x$  being  $x$  the nominal Co composition in the alloy. These compositions would lead to a magnetostriction constant  $\lambda$  of  $\sim 0$  and  $\sim 30$  ppm (Ref. 16) for the crystalline phase of Co5 and Co20 alloys, respectively. Therefore, considering that  $\lambda$  in the amorphous state is 18 and 36 ppm for Co5 and Co20 alloys, respectively,<sup>11</sup> a more effective decrease of the overall magnetoelastic anisotropy is expected in the alloy with the lowest Co content (while for Co5 alloy, a transformed volume ceases its contribution to the overall  $\lambda$ , for Co20 alloy, the crystallization of a volume unit produces only a decrease of  $\sim 17\%$  in its contribution to  $\lambda$ ). This effect could explain the observed differences in  $\mu$  at room temperature. As nanocrystallization progresses and the amorphous matrix becomes enriched in Zr and B atoms, the magnetization of this phase will decrease, causing a decrease in  $\lambda$ , assuming a correlation between both magnitudes.<sup>16</sup> This would produce



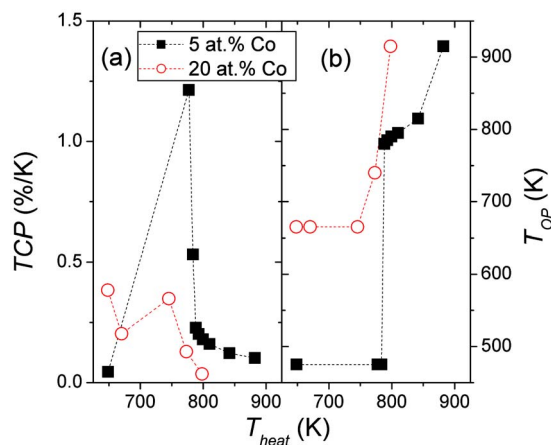


FIG. 3. (Color online) (a) Temperature coefficient of permeability (TCP) and (b) maximum temperature for application  $T_{op}$  as a function of the temperature at which the sample was previously heated  $T_{heat}$ .

that the effect of nanocrystallization on reducing the overall  $\lambda$  would become less effective as the nanocrystallization progresses and could even change from a decrease to an increase of the overall  $\lambda$ , explaining the worsening of the soft magnetic properties at room temperature for higher crystalline volume fractions.

In terms of technological applications at high temperature, the permeability value at room temperature is not the only important parameter. Another interesting parameter to consider is the temperature range of constant permeability, which can be described using the temperature coefficient of permeability (TCP) calculated as the relative change of permeability from 400 K to a maximum operative temperature  $T_{op}$  divided by the temperature span,  $\Delta T = T_{op} - 400$  K. For the amorphous samples,  $T_{op}$  is just below the Curie temperature and, for nanocrystalline samples,  $T_{op}$  is the maximum temperature at which no further microstructural evolution is expected. Values of TCP and  $T_{op}$  for samples of both alloys at different stages of devitrification are shown in Fig. 3.

The best reported TCP values for Fe-based soft magnetic nanocrystalline alloys were found for FeCoNbB(Cu) [0.01%/K (Ref. 17) and 0.02%/K (Ref. 7)] and FeCoMnNbBCu [ $\sim 0.05\%$ /K (Ref. 18)], with  $\Delta T$  extended up to 900 K. The maximum permeability reported among these alloys was  $\mu \sim 1000$ .<sup>7</sup> For the two systems subject of the present paper, the optimum values of TCP are 0.10%/K and 0.04%/K for Co5 and Co20 alloys, respectively, in a temperature range from room temperature up to 915 K. For applications, a compromise between TCP and  $\mu$  values should be found. Therefore, although TCP values of this paper are not better than the previously reported, the larger values of  $\mu$  make these alloys interesting for applications. In the case of 5 at.%

Co alloy, at room temperature and 6 kHz,  $\mu \sim 4000$  is four times larger than that of Fe<sub>39</sub>Co<sub>39</sub>Nb<sub>6</sub>B<sub>15</sub>Cu<sub>1</sub> alloy<sup>7</sup> and clearly larger than that of Fe<sub>44</sub>Co<sub>44</sub>Zr<sub>7</sub>B<sub>4</sub>Cu<sub>1</sub> at 0.4 kHz ( $\sim 1800$ );<sup>19</sup> TCP of Co5 is three times lower than that of Finemet<sup>20</sup> and a half and a quarter smaller than those of Nanoperm<sup>21</sup> and Co-doped Finemet alloys.<sup>22</sup>

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