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Structure and Thermomagnetic Properties of New FeCo-based Nanocrystalline Ferromagnets

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***Abstract*—FeCo-based ferromagnetic alloys (HITPERM variants) of composition $Fe_{44.5}Co_{44.5}Zr_7B_4$, $Fe_{44}Co_{44}Zr_{5.7}B_{3.3}Ta_2Cu_1$, $Fe_{44}Co_{44}Zr_{5.7}B_{3.3}Mo_2Cu_1$, and $Fe_{37.2}Co_{30.8}Zr_7B_4Cu_1$ were prepared by melt-spinning amorphous precursors, followed by nanocrystallization. Samples were characterized using vibrating sample magnetometry (VSM), x-ray diffraction (XRD), and differential scanning calorimetry (DSC). VSM was used to measure magnetization vs. temperature from 370–1260 K. Magnetic data showed structural and magnetic phase transitions including primary and secondary crystallization events and the to a structural phase transition in FeCo nanocrystals. Ta and Mo were observed to suppress the to a transition temperature of FeCo. The Fe : Co 65 : 35 alloy exhibits significant curvature in $M(T)$ indicating proximity of the ferromagnetic to paramagnetic transition and the α to γ transition. XRD phase analysis identified crystallized phases as α-FeCo, $(Fe,Co)_3Zr$, in agreement with previous reports for unmodified HITPERM alloys. DSC data, analyzed using the Kissinger technique, indicated that the removal of Cu from the original HITPERM composition increased the activation energy for primary crystallization, whereas Ta and Mo substitutions decrease the activation energy.**

***Index Terms*—FeCo alloys, nanocrystals, soft magnetic alloys.**

I. INTRODUCTION

NANOCRYSTALLINE soft magnets have superior soft magnetic properties stemming from chemical and structural variations on a nanoscale. We use the term *nanocrystalline* for alloys with grain diameters between 1–50 nm. Technologically important nanocrystalline magnets have been derived by crystallizing amorphous precursors of specific families of (Fe(Co),B)-based alloy chemistries. These materials have nanocrystalline grains of a (BCC or CsCl) (−(Fe(Co),X) phase consuming 70–90% of the total volume, homogeneously dispersed in an amorphous matrix. Therefore, two-phase materials are more appropriately designated as ***metal/amorphous nanocomposites***. Nanocrystalline alloys have impacted on industrial applications with the patenting of Fe–Si–B–Nb–Cu [1] alloys under the trade name FINEMET@™ and Fe–M–B–Cu [2] alloys under the trade name NANOPERM@™. Workers at CMU have discovered an important new nanocrystalline $(Fe_{1-x}Co_x)_{88}M_7B_4Cu_1$ ($M = \mathrm{Nb}$, Zr, Hf) soft magnetic material called HITPERM [3]–[5] with significant potential in high temperature and power electronic applications due to its frequency response and high temperature induction.

HITPERM is an $\alpha(\alpha')$-FeCo base alloy ($Fe_{44}Co_{44}Zr_7B_4Cu_1$) that exhibits an attractive combination of high Curie temperature (>1250 K), high saturation induction, (1.6 to 2.1 T), and excellent thermal stability. This alloy achieves its properties by coupling the high magnetic moment of the $\alpha(\alpha')$-FeCo system with reduced magnetic anisotropy (as explained by the random magnetic anisotropy model of Herzer [6]) of nanocrystalline alloys.

We report further development of HITPERM alloys and the influence of compositional variations. The goal of this work was to explore changes to the magnetic properties and nanocrystallization kinetics of the alloy caused by three types of compositional variations:

1) The first compositional variation consisted of changing the ratio of Fe to Co from 50 : 50 to 65 : 35. This was motivated by the fact that the 65 : 35 FeCo ratio is known to yield the highest saturation induction for transition metal alloys as depicted on the Slater–Pauling curve.
2) The second set of variations partially substituted the transition metals Ta and Mo for the glass forming elements Zr and B. These substitutions were studied to determine: a) changes in the crystallization and Curie temperatures of the amorphous alloy, b) changes in the α–γ structural phase transition temperature of the FeCo nanocrystals (which also corresponds to the ferromagnetic to nonmagnetic phase transition), and c) their effect on impeding the formation of undesirable secondary phases [2].
3) The third variation consisted of removal of Cu from the base HITPERM composition. Cu is believed to act as a nucleating agent and grain refiner due to its low solubility in Fe and Co [7], [8]. The effect of omitting Cu is observed in the activation energy of the primary crystallization event.

II. PROCEDURE

New compositions were first produced as precursor ingots by arc-melting the constituents under Ar. Ribbon samples were produced using a melt-spinning apparatus located at the Naval Research Laboratory. Some samples were crystallized by sealing them in evacuated silica tubes, annealing them at 873 K for 3600 s or 1023 K for 3600 s, followed by air cooling. Table I

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TABLE I
COMPOSITIONS AND EXPERIMENTAL OBSERVATIONS

Composition (atomic %)	T_{x1} (K)	$T_{\alpha\text{-}\gamma}$ (K)	Q (kJ/mol, eV/atom)
$Fe_{57.2}Co_{30.8}Zr_7B_4Cu_1$	748	1253	270, 2.80
$Fe_{44}Co_{44}Zr_{5.7}B_{3.3}Ta_2Cu_1$	753	1241	294, 3.05
$Fe_{44}Co_{44}Zr_{5.7}B_{3.3}Mo_2Cu_1$	736	1212	286, 2.96
$Fe_{44.5}Co_{44.5}Zr_7B_4$			365, 3.78
$Fe_{44}Co_{44}Zr_7B_4Cu_1$	753	1258	323, 3.35

lists the compositions that were examined, with the primary crystallization temperature (T_{x1}), α–γ transition temperature ($T_{\alpha-\gamma}$), and activation energy for primary crystallization. The last composition is the original HITPERM composition [1].

X-ray diffraction (XRD) with Cu Kα radiation was used to determine the structure of the alloy in the as melt-spun and annealed states. Diffraction patterns were collected from $2\theta = 30$ to 100°. Magnetization vs. temperature data was collected using a vibrating sample magnetometer (VSM) equipped with a vacuum electric furnace. The VSM was programmed to ramp at 2.2 K/min from 373 K to 1263 K at a constant field intensity of 41.8 kA/m (525 Oe). Differential scanning calorimetry (DSC) was used to observe the exothermic crystallization events during heat treatment. Primary crystallization temperatures were measured from DSC scans at heating rates of 5, 10, 20 and 40 K/min. A Kissinger [9] analysis was used to calculate activation energies by fitting data to the relation

$$\frac{d\left(\ln\left(\frac{\Phi}{T_{x1}^2}\right)\right)}{d\left(\frac{1}{T_{x1}}\right)} = -\frac{E}{R} \tag{1}$$

in which Φ is the heating rate, T_{x1} the primary crystallization temperature, R the ideal gas constant, and E the activation energy.

III. RESULTS

XRD verified that all the samples were amorphous in the as-melt-spun state. Subsequent to annealing at 873 K α-FeCo phases were found (it is not possible to distinguish between the A2 disordered and B2 ordered FeCo structures due to the similar x-ray scattering factors of Fe and Co). Subsequent to annealing at 1023 K secondary phases such as ZrB_2 and $(Fe, Co)_{23}Zr_6$ were identified in all samples. Secondary phases containing Ta or Mo were not identified.

Fig. 1 presents the magnetization v. temperature curves normalized to magnetization at 373 K. Magnetization of the amorphous as-spun samples is seen to steadily decrease to what would be the amorphous Curie temperature. In all samples the primary crystallization event is clearly indicated by a sharp increase in magnetization at about 748 K. Evidence for secondary crystallization may be apparent in the base HITPERM and Ta-modified compositions, but is absent in the remaining compositions The α–γ transition is indicated by a loss of magnetization between 1223 K and 1253. Primary crystallization temperatures and α–γ transition temperatures are presented in Table I.

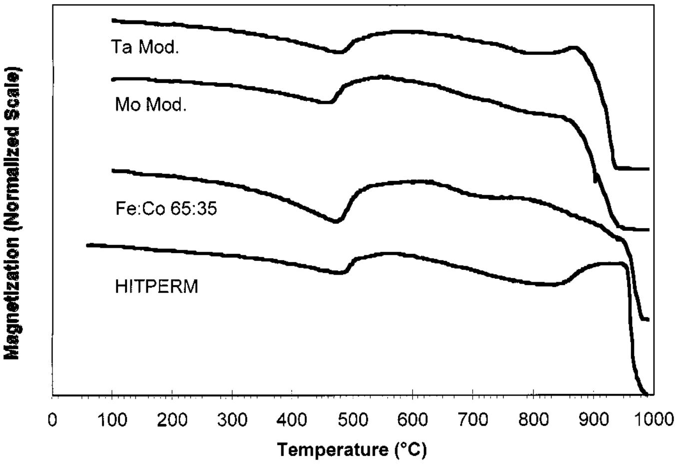

Fig. 1. Magnetization as a function of temperature. Measurements were made by vibrating sample magnetometry at a constant field of 42 kA/m (525 Oe) while sweeping temperature from 372–1260 K at a constant rate of 2.2 K/min. All curves normalized to magnetization at 373 K. For clarity, each curve displaced along the vertical axis.

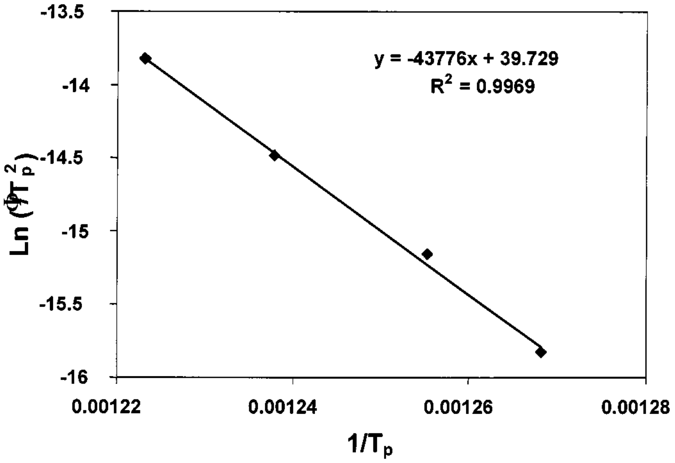

Fig. 2. Kissinger plot of $Fe_{44.5}Co_{44.5}Zr_7B_4$ from DSC scans performed at heating rates (Φ) of 5, 10, 20, and 40 K/min. Peak temperature (T_p) measured as absolute temperature. Slope corresponds to an activation energy of 363 kJ/mol, or 3.78 eV/atom.

Fig. 2 presents the Kissinger plot for the non-Cu containing composition. Excellent linearity is observed ($R^2 > 99\%$). When fit to (1) this line yields the activation energy in J/mol. Table I presents the primary crystallization activation energies computed from Kissinger analysis of the DSC data. For each composition the activation energy for the base HITPERM composition is listed for comparison. The removal of Cu is observed to increase the activation energy. The substitution of Ta or Mo is observed to decrease the activation energy.

IV. DISCUSSION

Extrinsic magnetic properties, such as coercivity and permeability, depend on the microstructure of the ferromagnetic alloy. The microstructure, in turn, depends sensitively on the thermal and magnetic history of the samples. Key to the magnetic properties of these alloys is their nanometer-scale grain size. Bulk FeCo has an undesirably large coercivity and large core loss for AC applications. A nanometer scale grain size is on the order of the ferromagnetic exchange length. Hence, magnetocrystalline anisotropy is averaged over many grains and the coercivity is reduced [6]. An additional contribution to AC power loss is magnetostriction (λ).

HITPERM based compositions display three structures depending upon thermomagnetic history. In the as-spun state the structure is an amorphous. After primary crystallization the structure consists of α-FeCo particles surrounded by a Zr and B rich amorphous intergranular phase. This phase remains ferromagnetic well above the primary crystallization temperature. This is important in maintaining ferromagnetic exchange between adjacent grains. The Curie temperature of the residual amorphous phase is expected to differ from the parent phase due to segregation of Zr and B to the grain boundaries. Secondary crystallization results in secondary phases precipitating from solution. The secondary phases did not appear to be compounds of Ta or Mo. However, they are expected to increase coercivity by impeding domain wall motion, either as nonmagnetic inclusions or highly anisotropic ferromagnetic particles.

The primary crystallization temperature did not appear to be affected by the composition variations. However, the α–γ phase transition was noticeably reduced for the Ta- and Mo-modified compositions. The equilibrium FeCo phase diagram indicates that this phase transition occurs at 1258 K for the $\mathrm{Fe}_{55}\mathrm{Co}_{45}$ composition. This temperature is in general agreement with the our measurements of the base HITPERM and Fe : Co 65 : 35 variant. The Fe–Ta and Fe–Mo phase diagrams suggest that Ta and Mo should act as α-stabilizers, that is, they should raise the α–γ transition temperature. However, it must be realized that this transition is a first order structural phase transformation. The second order ferromagnetic to paramagnetic transition temperature for α-FeCo has been calculated to occur at a temperature greater than 1500 K [10]. Light transition metal impurities in the series Ti through Cu are known to reduce the atomic magnetic moment of α-FeCo [11]. This can be qualitatively understood through a change in the filling of states in a Freidel model. Mean field theory predicts the Curie temperature generally scales with the magnetic moment [12].

It is to be expected then that the Curie temperature would change with composition below the solubility limit of Ta or Mo in Fe(Co). It would be instructive to perform band structure calculations to determine the density of states for α-FeCo with heavier transition metals such as Ta and Mo, as well as the influence of these elements on the Fe(Co) exchange interactions. Atomic moments could then be calculated and Curie temperatures estimated within a mean field theory description.

The role of Cu as a nucleating agent and grain refiner in nanocrystalline alloys has been a topic of interest [7], [8]. The proposed mechanism concerns the low solubility of Cu in Fe causing it to precipitate from the amorphous phase. In this work, we have observed a marked increase in the activation energy of the primary crystallization event with the absence of Cu. Interestingly, the presence of a transition metal lowers the activation energy. This may be due to a similar mechanism to Cu, since transition metals such as Ta have low equilibrium solubility in Fe.

V. CONCLUSION

Changing the ratio of Fe and Co from 50 : 50 to 65 : 35 changes the temperature dependence of the amorphous magnetization without affecting the primary crystallization temperature or the α–γ transition temperature. The partial substitution of Ta or Mo does not affect the primary crystallization temperature but does reduce the α–γ transition temperature. The activation energy of primary crystallization has been shown to increase with the absence of Cu and decrease with the presence of a transitition metal.

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