Processing of Alnico Permanent Magnets by Advanced Directional Solidification Methods

Zou, Min¹; Johnson, Francis¹; Zhang, Wanming¹; Zhao, Qi¹; Rutkowski, Stephen F.¹;

Zhou, Lin^{2, 3}; Kramer, Matthew J.^{2, 3}

¹Ceramic and Metallurgy Technologies, General Electric Global Research, Niskayuna, NY, United States

²Ames Laboratory, Ames, IA, United States

³Iowa State University, Ames, IA, United States

Abstract

Advanced directional solidification methods have been used to produce large (>15 cm length) castings of Alnico permanent magnets with highly oriented columnar microstructures. In combination with subsequent thermomagnetic and draw thermal treatment, this method was used to enable the high coercivity, high-Titanium Alnico composition of 39% Co, 29.5% Fe, 14% Ni, 7.5% Ti, 7% Al, 3% Cu (weight %) to have an intrinsic coercivity (H_{ci}) of 2.0 kOe, a remanence (B_r) of 10.2 kG, and an energy product $(BH)_{max}$ of 10.9 MGOe. These properties compare favorably to typical properties for the commercial Alnico 9. Directional solidification of higher Ti compositions yielded anisotropic columnar grained microstructures if high heat extraction rates through the mold surface of at least 200 kW/m² were attained. This was achieved through the use of a thin walled (5 mm thick) high thermal conductivity SiC shell mold extracted from a molten Sn bath at a withdrawal rate of at least 200 mm/hour. However, higher Ti compositions did not result in further increases in magnet performance. Images of the microstructures collected by scanning electron microscopy (SEM) reveal a majority α phase with inclusions of secondary α_γ phase. Transmission electron microscopy (TEM) reveals that the α phase has a spinodally decomposed microstructure of FeCo-rich needles in a NiAl-rich matrix. In the 7.5% Ti composition the diameter distribution of the FeCo needles was bimodal

with the majority having diameters of approximately 50 nm with a small fraction having diameters of approximately 10 nm. The needles formed a mosaic pattern and were elongated along one $\langle 001 \rangle$ crystal direction (parallel to the field used during magnetic annealing). Cu precipitates were observed between the needles. Regions of abnormal spinodal morphology appeared to correlate with secondary phase precipitates. The presence of these abnormalities did not prevent the material from displaying superior magnetic properties in the 7.5% Ti composition. Higher Ti compositions did not display the preferred spinodal microstructure, explaining their inferior magnetic properties.

Keywords: Alnico; directional solidification; permanent magnets; transmission electron microscopy.

I. INTRODUCTION

Alnico permanent magnets have attracted revived interest since the recent spike in rare earth element prices. [1]-[5]. Stoner-Wohlfarth theory predicts a maximum energy product $(BH)_{\max}$ of 49 MGOe for a 67 vol.% packed $\text{Fe}_{65}\text{Co}_{35}$ nanostructure, given the FeCo nanowires do not exceed the coherence radius of the order of 10 nm [6]. The highest energy products achieved in Alnico permanent magnets, however, are 13.4 and 9.0 MGOe, in laboratory and commercial grades Alnico 9, respectively, with an intrinsic coercivity (H_{ci}) of 1.5 kOe [7]. The highest H_{ci} in commercial Alnico is 2.2 kOe in Alnico 8H with an energy product of 5.0 MGOe [8]. The major difference between the Alnico 8H and 9 compositions is that 8H has higher Co and Ti contents. It has been reported that high Ti content favors the high coercivity but impedes the formation of the columnar grain structure, thus degrading the remanence (B_r) and energy product [7]. For example, the commercial Alnico 9 with a 5 wt.% Ti has a columnar grain structure, but the Alnico 8H with a 7.5 wt.% Ti is randomly grained [4]. The columnar grain structure has been reported in 7.5% Ti using the controlled cooling method with a speed of 5mm/hr [9], and in 8.2% Ti without disclosure of casting details [10]. No literature report can be found on successful casting of Ti composition higher than 8.2% with a columnar microstructure. This study explores the application of advanced directional solidification casting methods to 7.5 % and higher Ti (9% and 12%) compositions in order to form highly oriented columnar microstructures to improve the B_r and energy products and maintain or improve the high H_{ci} in these compositions.

II. EXPERIMENTAL DETAILS

Master ingots of three compositions of Alnico were cast by vacuum induction melting. Three casts were prepared in an ALD VIM-IC liquid metal cooled vacuum investment casting furnace using molds with cavity dimensions of $150 \times 38 \times 38 \text{ mm}^3$. Liquid tin (Sn) was used as the coolant medium. The alloy compositions, mold parameters, and casting conditions are listed in TABLE I.

The as-cast alloys were cut into $15 \times 10 \times 2 \text{ mm}^3$ slices from the middle sections of the ingots. One slice for each composition was etched using Marble etchant (10 g CuSO_4 in 50 ml HCl + 50 ml H_2O solution) for a few seconds to reveal dendritic structures evaluated using the LEO 1450VP SEM and KEYENCE VHX-600 light microscope. Other slices were solution heat treated at different solutionization temperatures and time durations chosen as the ones to yield least secondary phase volume fractions based on the SEM data. The solutionized alloys were then cut into $\approx 4 \times 2 \times 2 \text{ mm}^3$ parallelepipeds for thermomagnetic and draw cycle treatments in a magnetic field of 2.7 kOe applied along the columnar grain direction at different temperatures and time durations optimized for different alloy compositions exhibiting the highest H_{ci} . In particular, because the spinodal decomposition temperature of each alloy composition was unknown, the magnetothermal treatments were carried out first at an estimated spinodal decomposition temperature (T_1) for 10 minutes, then at temperatures 20 °C higher (T_2) and lower (T_3) than T_1 . The H_{ci} of the samples heat treated at these three temperatures were then measured. If the H_{ci} of the sample heat treated at T_2 was greater than that at T_1 , then the next heat treatment was set at a temperature 20 °C higher than T_2 . If the H_{ci} of the sample heat treated at T_3 was greater than that at T_1 , then the next heat treatment was set at a temperature 20 °C lower than T_3 . The H_{ci} of each sample after every heat treatment was measured and compared, until a highest H_{ci} was observed at a particular temperature (T_n) for a specific alloy composition. Then the thermomagnetic treatments were carried out at temperatures 10 °C higher and lower than T_n . The H_{ci} of the two samples were compared, and the temperature at which yielded the highest H_{ci} was determined as the optimal thermomagnetic treatment temperature (T_o) for the alloy composition. Then the same method was used to vary the heat treatment time between 1 and 120 min at T_o for each alloy composition. The two-step draw cycle treatments were also optimized between 500 and 675 °C and between 6 and 48 hours in the same manner.

The magnetic properties of the heat treated samples were measured using a Quantum Design Physical Property Measurement System (PPMS) Model 6000 equipped with a vibrating sample magnetometer (VSM). The demagnetization factors were corrected using the equation derived in [11] by cutting samples

into rectangular specimens and carefully measuring their dimensions. The appropriately-corrected open-loop measurements were estimated to agree with closed-loop measurements to within $\pm 3\%$ error [12].

Transmission electron microscopy (TEM) analysis was performed on transverse sections (with electron beam parallel to H direction) and on longitudinal orientation (with electron beam perpendicular to H direction) on a FEI Tecnai F20. TEM samples were prepared by mechanical wedge-polishing followed by a short time, low voltage Ar ion-milling with liquid nitrogen cold stage.

III. RESULTS AND DISCUSSION

The columnar grained microstructures are clearly evident in the optical images of the three alloys as shown Fig. 1.

For 1-D steady state directional solidification (DS), the liquid thermal gradient G_L is expected to increase as the melt temperature T_{melt} decrease, based on the heat balance equation,

$$G_L = \frac{k_S G_S - \rho_{\text{melt}} [H_f + C_{p,\text{melt}} (T_{\text{melt}} - T_L)] R}{k_L} \quad (1)$$

where G_L and G_S are liquid and solid thermal gradients at the liquid-solid interface, k_S and k_L are liquid and solid metal thermal conductivities, ρ_{melt} and $C_{p,\text{melt}}$ are melt density and specific heat, T_L and H_f are alloy liquidus temperature and latent heat, and R the liquid-solid interface growth rate [13]. At a given solidification rate, a higher G_L enhances DS growth in the $\langle 001 \rangle$ direction, which is coincident with Alnico easy direction for magnetization. The higher the G_L is, the lower the misorientation and the stronger the $\langle 001 \rangle$ texture is.

Replacing solid heat flux $k_S G_S$ with DS heat extraction rate, Q_{DS} , Eq. (1) can be rewritten as Eq. (2),

$$G_L = \frac{Q_{\text{DS}} - \rho_{\text{melt}} [H_f + C_{p,\text{melt}} (T_{\text{melt}} - T_L)] R}{k_L} \quad (2)$$

For given casting design and withdraw rate V for a given alloy, G_L increases as Q_{DS} increases and T_{melt} decreases. If assuming steady state growth and constant thermal boundary conditions, Q_{DS} as a function of withdrawal length L , can then be expressed in Equations (3), (3a), and (4)

$$Q_{DS}(L) = \frac{q_{z,0}[T_m(L)-T_{chill}]}{[T_s-T_{chill}]} + \frac{2(W+D)}{WD} \int_0^{L=Vt} q_{ex}(z)dz \quad (3)$$

$$= \frac{q_{z,0}[T_m(L)-T_{chill}]}{[T_s-T_{chill}]} + \frac{1}{m_c} \int_0^{L=Vt} q_{ex}(z)dz \quad (3a)$$

$$q_{ex} = h_{eff}(L)[T_{m,surf}(L) - T_{amb}] \quad (4)$$

where $q_{z,0}$ is initial heat flux through casting/mold support interface in withdrawal direction, $T_m(L)$ is casting temperature at mold support contact interface, T_{chill} is mold support temperature, T_s is solidus temperature, W and D are width and thickness of the DS ingot, q_{ex} is heat extraction rate normal to the vertical shell surface, m_c is casting modulus (volume to surface ratio), t is withdrawal time, h_{eff} is an effective heat transfer coefficient, $T_{m,surf}$ is metal surface temperature, and T_{amb} is surrounding environment temperature. With certain approximations, h_{eff} in Eq. (4) can be expressed in Equation (5) [14],

$$\frac{1}{h_{eff}} = \frac{D}{2k_s} + \frac{1}{h_{gap}} + \frac{t_{shell}}{k_{shell}} + \frac{1}{h_{surf}} \quad (5)$$

where k_{shell} and t_{shell} are equivalent shell thermal conductivity and shell thickness, h_{gap} is heat transfer coefficient at metal-shell gap depending on $T_{m, surf}$, and h_{surf} is heat transfer coefficient at shell surface depending on $T_{s, surf}$ in general. Per Eq. (3), Q_{DS} increases with shell surface cooling rate, casting surface area, withdrawal rate and time, but decreases as casting volume increases. Substituting Eqs. (3), (4), and (5) into Eq. (2), an analytical description of G_L dependency on casting parameters, cooling rate, part geometry and withdrawal length (or time) can be expressed in Equation (6),

$$G_L = \frac{q_{z,0} \left(\frac{T_m(L)-T_{chill}}{T_s-T_{chill}} \right) + \frac{1}{m_c} \int_0^{Vt} q_{ex}(z)dz - \rho_{melt}[H_f + C_{p,melt}(T_{melt}-T_L)]R}{k_L} \quad (6)$$

Assuming $R=V$, Equations (3) and (6) were solved numerically with iterations for Alnico bar castings of 38×38mm in cross section. The maximum horizontal shell surface heat extraction rate of the advanced SiC shell liquid metal cooling (LMC) process is then estimated as 230KW/m², compared to about 63KW/m² for the conventional Bridgman process, and 127KW/m² for the conventional LMC process.

Thin-walled SiC stucco-coated molds were developed and used for the 9% Ti and 12% Ti compositions [15], [16]. The measured thermal diffusivities and converted thermal conductivities show that the SiC shell

has a 350% higher thermal conductivity than its alumina counterpart. The high thermal conductivity of the SiC shell mold and the low melt temperature (~ 100 °C above their melting points determined from differential scanning calorimetry) in the casting method, enabled the formation of columnar structures in these high Ti compositions with a high withdraw rate, 152 and 203 mm/hr, much faster than the earlier report of 5mm/hr [9].

The composition heterogeneity as evident in Fig. 1 was mostly eliminated after solution heat treatment. The microstructures collected by SEM reveal a majority α phase with inclusions of secondary α_γ phase, as shown in Fig. 2 (a) to (c) as the light grey areas. The α_γ phase mostly segregated in the grain boundaries and it persists even in the subsequently magnetically annealed samples exhibiting the best B_r , H_{ci} , and $(BH)_{max}$, as shown in Fig. 2 (d).

The best magnetic properties of each composition post magnetic field annealing are shown in TABLE I. The 7.5%Ti composition exhibits high saturation magnetization (M_s), B_r , H_{ci} , and $(BH)_{max}$, which compare favorably to typical properties of commercial grades high $(BH)_{max}$ Alnico 9 and high H_{ci} Alnico 8H. The higher Ti composition in 9% Ti leads to a higher H_{ci} , but lower M_s and B_r , causing an inferior $(BH)_{max}$. In the 12% Ti composition, all magnetic properties are inferior.

TEM images shown in Fig. 3 were collected on the samples with their magnetic properties listed in TABLE I. The images demonstrate that the α phase is spinodally decomposed into a microstructure of FeCo-rich needles in a NiAl-rich matrix. In the 7.5% Ti composition the diameter distribution of the FeCo needles is bimodal with the majority having diameters of approximately 50 nm and a small fraction having diameters of approximately 10 nm, as shown in Fig. 3(b). The needles formed a mosaic pattern and a diamond shape viewed from the cross section as shown in Fig. 3(a) and (b), and were elongated along a $\langle 001 \rangle$ crystal direction (parallel to the field used during magnetic annealing), as illustrated in Fig. 3(c) and (d). Cu precipitates were observed between the needles, as marked in the Fig. 3(b) and (d). TEM images collected on the transverse [Fig. 3 (a) and (b)] and longitudinal [Fig. 3(c) and (d)] to the orientations illustrate the strongly anisotropic spinodal structure of the 7.5% Ti composition, which explains the high B_r

observed in this composition.

Increasing Ti content to 9%, the bimodal FeCo precipitates still form a mosaic pattern, but compared with the 7.5% Ti composition, the small FeCo precipitates grow both in number and size, and the large FeCo precipitates grow slightly smaller, as shown in Fig. 3(e) to (h). The FeCo-rich phase volume fraction in 9% Ti qualitatively appears to be smaller than that in the 7.5% Ti. This may account for the 10% increase of H_{ci} in the 9% Ti composition, considering $H_c(p) = H_c(0)(1-p)$, where p is the volume fraction of the FeCo-rich phase, and $H_c(0)$ is the coercivity of the single FeCo rich particle, $H_c(p)$ is the coercivity of the alloy [7]. Another distinct difference between the 9% and 7.5% Ti compositions lies in their longitudinal morphologies. Instead of the majority of elongated FeCo needles are evenly and separately distributed in the NiAl matrix as shown in Fig. 3(c) and (d) in 7.5% Ti, the FeCo needles are perpendicularly cross linked for 9% Ti as shown in Fig. 3(g) and (h). Although the 9% Ti was successfully cast to a columnar structure, unfortunately, the applied magnetic field fails to efficiently align the FeCo precipitates along the columnar grain direction. The nearly isotropic alignment of the FeCo precipitates are likely responsible for the nearly 50% drop of the B_r of 9% Ti from the 7.5% Ti.

Further increasing the Ti content to 12%, the spinodal microstructure shown in Fig. 3 (i) to (l) losses both mosaic pattern and anisotropy. Although the diameter and volume fraction of the FeCo precipitates reduce further, the cross linked FeCo needles may interact strongly with each other during the magnetization reversal, leading to a 35% drop of H_{ci} from 7.5% Ti composition. The B_r of 12% Ti reduces 26% further from 9% Ti due to the further reduced FeCo alignment anisotropy.

Regions of secondary phase precipitates and abnormal spinodal morphology were observed in TEM images of 7.5%, 9%, and 12% Ti compositions. Fig. 4 shows representative images collected in the 7.5% Ti composition. The interruption of the mosaic pattern and variation of the diameters and distances between the FeCo needles are evident in the vicinity of the secondary phase precipitates as shown in Fig. 4(b). The presence of these abnormalities, however, did not prevent the material from displaying superior magnetic properties most likely due to their low volume fraction.

IV. CONCLUSION

Advanced directional solidification methods were applied to Alnico with Ti concentrations of 7.5, 9, and 12 wt.%. Low melt temperature and high thermal gradient achieved via thin-walled high thermal conductivity SiC shell mold enable the formation of highly oriented columnar grain structure in these high Ti compositions. Combined with appropriate magnetic field annealing, the 7.5% Ti composition measures H_{ci} of 2.0 kOe, B_r of 10.2 kG, and energy product of 10.9 MGOe, surpassing those of the commercial Alnico magnets. The unidirectionally elongated and distinctly separated FeCo needles and the uniform bimodal size distribution of these needles are responsible for its superior magnetic performance. The 9% Ti composition exhibits a high H_{ci} of 2.2 kOe, originated from the preservation of the bimodal mosaic microstructure. The B_r of the 9% Ti composition, however, drops almost 50% from the 7.5% Ti composition because the alignment of the FeCo needles becomes more isotropic. The microstructure of the spinodally decomposed 12 % Ti composition loses both the mosaic pattern and unidirectional elongation of the FeCo precipitates, yielding a 35%, 60%, and 87% reduction of the H_{ci} , B_r , and $(BH)_{max}$ from 7.5% Ti. The inability of the applied magnetic field to effectively align the FeCo precipitates in the 9% and 12% Ti compositions is suggested to originate from a greater degree of separation of the spinodal decomposition and Curie temperatures in those compositions.

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Sample ID		7.5% Ti	9% Ti	12% Ti
wt. %	Al	7	8	7
	Ni	14	14	14
	Fe	29.5	26.6	25.5
	Co	39	39.4	39
	Cu	3	3	3
	Ti	7.5	9	12
Face coat stucco		Alumina	Alumina	Alumina
Backup stucco		Alumina	Hi-K SiC	Hi-K SiC
Shell thickness		5mm	5mm	5mm
Melt temp. (°C)		1430	1430	1430
Withdraw rate (mm/hr)		152	203	203
M_s (kG)		11.0	9.2	8.7
B_r (kG)		10.2	5.4	4.0
H_{ci} (kOe)		2.0	2.2	1.3
$(BH)_{max}$ (MGOe)		10.9	3.2	1.4

TABLE I. Compositions, mold and casting conditions, and magnetic properties of the alnico alloys processed by directional solidification methods and subsequent magnetic field annealing.

Fig. 1. Optical images of the as-cast Alnico with (a) 7.5%, (b) 9%, and (c) 12% Ti compositions produced by advanced directional solidification methods. The vertical arrows mark the directional solidification direction.

Fig. 2. Back scattered SEM images of solution heat treated (a) 7.5% Ti, (b) 9% Ti and (c) 12% Ti compositions, and (d) magnetic field annealed 7.5% Ti composition produced by advanced directional solidification methods.

Fig. 3. TEM images of magnetic field annealed (a) to (d) 7.5% Ti, (e) to (h) 9% Ti, (i) to (l) 12% Ti compositions produced by advanced directional solidification methods. The $\perp$ and $//$ symbols on the top right corner of each image mark the orientation (transverse and longitudinal, respectively) to the magnetic field applied during annealing.

Fig. 4. TEM images of magnetic field annealed 7.5% Ti composition produced by advanced directional solidification methods. The $\perp$ and $//$ symbols on the top right corner of each image mark the transverse and longitudinal viewing orientations of the images, respectively. The transverse section at a) lower magnification and b) higher magnification show disruption of the normal mosaic pattern.

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