ATOMIC LEVEL CHARACTERIZATION OF THE MORPHOLOGY OF PHASES IN CHROMINDUR MAGNETIC ALLOYS

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ABSTRACT

The atom probe field ion microscope has been used to characterize the morphology and determine the compositions of the iron-rich α and chromium-enriched α' phases produced during isothermal and step cooled heat treatments in a Chromindur II ductile permanent magnet alloy. The good magnetic properties of this material are due to a combination of the composition of the two phases and the isolated nature and size of the ferromagnetic α phase. The morphology of the α phase is produced as a result of the shape of the miscibility gap and the step-cooled heat treatment and is distinctly different from that formed during isothermal heat treatments.

INTRODUCTION

The Fe-Cr-Co ternary alloys provide the basis for a series of ductile permanent magnet alloys known as Chromindur. These alloys develop their good magnetic properties through phase separation within a low temperature miscibility gap. Aging these alloys within the low temperature miscibility gap results in decomposition of the solid solution into a ferromagnetic iron-rich α phase and a paramagnetic or weakly ferromagnetic chromium-enriched α' phase. The cobalt increases the critical temperature of the miscibility gap and also improves the magnetic properties of the alloy.

In this study the morphology and composition of these phases has been determined with an energy-compensated atom probe field ion microscope. This atomic resolution instrument is well suited to characterization of these materials due to the fine scale and complex morphology of the decomposition. The serial sectioning capability of this instrument permits the morphology of phases to be reconstructed in three dimensions.^[1]

EXPERIMENTAL

The material used in this investigation was a commercial Chromindur II alloy. The nominal composition of this alloy is given in Table 1. The alloy was examined after both step cooled and isothermal aging treatments. The alloy was solution treated above the miscibility gap at 920°C for 0.5 h and water quenched. The step-cooled heat treatment was 3 h at 620°C (SC1), 1 h at 600°C (SC2), 2 h at 580°C (SC3), 2 h at 560°C (SC4) and 1.5 h at 540°C (SC5). The alloy was water quenched to room temperature after each aging step. Samples were characterized after each aging step. Isothermal aging treatments were conducted at 600°C and 560°C for times up to 100 h. The alloy was water quenched to room temperature after each treatment.

All atom probe analyses were performed in the Oak Ridge National Laboratory energy-compensated atom probe.^[2] The field ion micrographs were recorded with neon as the image gas and specimen temperatures between 70 and 90K. Atom probe analyses were performed at 60K.

The magnetic coercivity measurements were obtained with a vibrating magnetometer. A saturation field of -1.3 MA m^{-1} (16 KOe) was applied during the measurements.

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TABLE 1. NOMINAL COMPOSITION OF CHROMINDUR II

Element	wt. %	at. %
Chromium	28.5	30.1
Cobalt	10.6	9.9
Nickel	0.36	0.34
Manganese	0.12	0.12
Silicon	0.08	0.16
Iron	bal.*	bal.*

(*residual elements not shown)

RESULTS

Coercivity and Hardness

The results of the coercivity measurements for the step-cooled and isothermal heat treatment at 560°C are given in Table 2.^[3] The coercivity of the as-quenched condition was 0.9 kAm⁻¹. These results indicate that there is a small increase in coercivity from 0.9 to 3.5 kAm⁻¹ as phase decomposition occurs at 600°C and a progressive increase as the aging temperature is reduced. The step-cooled heat treatment produces a considerably larger coercivity than the isothermal heat treatment.

TABLE 2. COERCIVITY AND HARDNESS RESULTS OF THE STEP COOLED AND ISOTHERMAL HEAT TREATMENTS

Code	Heat Treatment		Coercivity kAm ⁻¹	Hardness VHN
ST	0.5 h	920°C	0.9	
SC1	ST + 3 h	620°C	3.5	290
SC2	SC1 + 1 h	600°C	3.2	295
SC3	SC2 + 2 h	580°C	12.8	338
SC4	SC3 + 2 h	560°C	20.8	365
SC5	SC4 + 1.5 h	540°C	27.7	377
Isothermal	2 h	560°C	0.9	
Isothermal	100 h	560°C	2.7	

Microstructure

A pair of field ion micrographs of an isothermally aged specimen (8 h at 600°C) and a step cooled specimen (SC5) is shown in Fig. 1. Atom probe analysis revealed that the darkly-imaging regions are the chromium-enriched α' phase and the brightly-imaging regions are the iron-rich α phase. In the isothermally aged material, the microstructure consists of a complex interconnected network structure similar to that previously observed in Fe-Cr binary alloys.^[4,5] In this network structure, both the α and α' phases are essentially fully contiguous and may be regarded as one particle in each grain. The scale of the α phase in the step-cooled heat treatment was larger than that observed in the isothermal heat treatment. Field ion micrographs from the solution treated condition and the step-cooled heat treatments are shown in Fig. 2. No phase separation was evident in the solution treated condition. Extensive field evaporation sequences of the step cooled conditions revealed that at 620°C the iron-rich phase forms irregularly-shaped extended but isolated particles in the chromium-enriched matrix. As the temperature is lowered, the α phase coarsens and some coalescence of these particles occurs at the later stages of the heat treatment. Some secondary α phase was observed in the α' phase in the SC4 and SC5 stages.

The volume fractions of the two phases were determined from sequences of field ion

Fig. 1. Comparison of field ion micrographs of Chromindur II alloy (A) isothermally aged for 8 h at 600°C and (B) step cooled to 540°C (SC5). Dark regions are α' phase.

ST

SC1

SC2

SC3

SC4

SC5

Fig. 2. Field ion micrographs of the solution treated (ST) and step cooled (SC1 through SC5) materials.

micrographs and the results are given in Table 3. These volume fraction results indicate that the iron-rich α phase is the minor phase after the first stage heat treatment (SC1), but as the step-cooling treatment continues at lower temperature the volume fraction of the α phase increases and it becomes the major phase.

TABLE 3. VOLUME FRACTION OF THE IRON-RICH α PHASE

Heat Treatment	Volume Fraction, %
SC1	41 $\pm$ 9.6
SC2	60 $\pm$ 3.8
SC3	65 $\pm$ 4.2
SC4	67 $\pm$ 1.9
SC5	68 $\pm$ 2.3
8 h at 600°C	65 $\pm$ 7.5

Composition

An atom probe composition profile through the two phase microstructure in the isothermally aged alloy is shown in Fig. 3. The phase separation into the chromium-enriched α' and iron-rich α phase and the partitioning of Co to the iron-rich α phase is clearly evident. Contingency table analysis of the atom probe composition data revealed that the Fe and Co were strongly partitioned ($\chi^2=740$ with 54 degrees of freedom) and Cr and Co were antipartitioned ($\chi^2=677$ with 54 degrees of freedom). Atom probe selected area analyses of the α and α' phase for the step-cooled heat treatments are summarized in Table 4. A significant variation in the composition of the α phase from the central region to the α/α' interface was observed indicating that the partitioning of the Cr and Co was not complete. A progressive increase in chromium in the α' and a decrease in the α phase with aging treatment was observed. Statistical analysis of the composition data with the P_s method confirmed that phase separation had occurred at all stages of the step cooled heat treatment (e.g. $P_s = 0.126$ after SC1: where $2P_s$ may be defined as the amplitude of the composition fluctuations).

Fig. 3. Atom probe composition profile through the α/α' microstructure in the isothermally alloy aged 8 h at 600°C.

The Co level decreases in both phases during the step-cooled heat treatment. This unusual behavior arises because of the increase in the volume fraction of the α phase that also occurs with decreasing temperature and this requires that the Co level decrease in the α phase to maintain a Co mass balance. The ratio of Co to Fe in the α phase was also found to decrease with decreasing temperature. A comparison of the chromium levels of the α' phase in the step-cooled heat treatment (Cr < 62.6%) and the isothermal treatment at 600°C (Cr = 71%) and previous atom probe data on the 560°C isothermal heat treatment (Cr = 80% after 8 h)^[6] revealed that complete phase separation or metastable equilibrium had not been attained for all stages at 600°C or below.

TABLE 4. AVERAGE Cr AND Co LEVELS IN THE α AND α' PHASES

Heat Treatment	α phase		α' phase	
	Cr	Co	Cr	Co
SC1	13.2	15.8	35.0	7.7
SC2	7.4	15.0	40.4	5.7
SC3	7.5	14.4	42.9	5.6
SC4	7.7	12.6	60.1	3.3
SC5	5.2	13.5	62.6	3.0
8 h at 600°C	5.2	15.1	71.0	3.5

CONCLUSIONS

Since the composition and volume fraction of the α phase are similar in the step-cooled and isothermal heat treatments, the difference in the magnetic properties is a result of the difference in morphology and scale of the α phase.

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