The Effect of Titanium on Microstructure and Magnetic Properties of Fe-Cr-Co Hard Magnetic Materials

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The effect of titanium on microstructure and magnetic properties of Fe-Cr-Co hard magnetic materials

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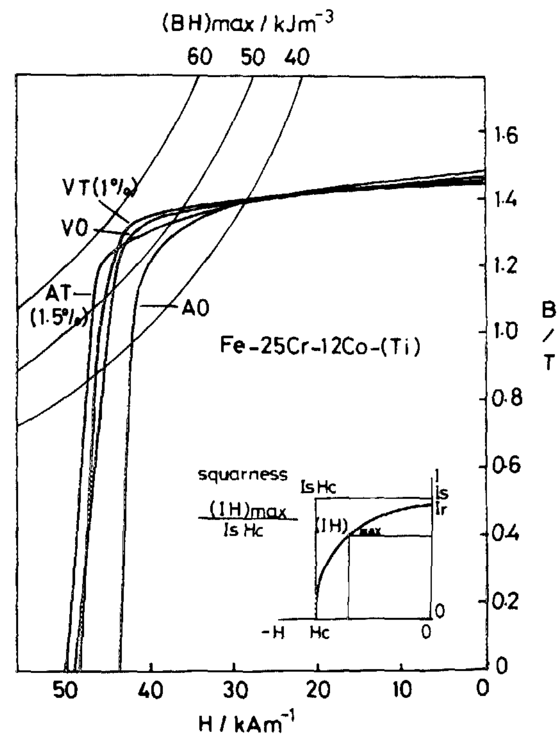
Fe-Cr-Co ductile alloys produce magnetic properties comparable to those of Alnico permanent magnets family, up to $(BH)\max = 91.2\ \mathrm{kJ/m^3}$(11.4 MGOe). It is technologically known that the addition of Ti to the Fe-Cr-Co alloys extends the α-phase region of system and improves the magnetic properties. The purpose of this work is to study the effect of Ti on microstructures and magnetic properties of Fe-Cr-Co alloys. The microstructures of Fe-25 wt.% Cr-12 wt.% Co alloys with or without Ti melted in air or in vacuum, were studied by optical microscopy, electron probe microanalysis (EPMA), and transmission electron microscopy (TEM). The alloys without Ti exhibit the precipitates of $Cr_{23}C_6$ carbide and Cr_2N nitride *a* along the grain boundary or inside grain. These carbides and nitrides form the Cr-depleted zone around them. However, the addition of Ti suppressed the formation of Cr-depleted zone, in forming the Ti(C,N), and the magnetic properties are improved.

I. INTRODUCTION

Fe-Cr-Co alloys are potential magnets because of their good ductility and excellent magnetic properties comparable to those of Alnico magnets family.[1-10] Fe-Cr-Co alloys can provide expanded applications for high-performance small magnet circuits, which are difficult to make with Alnico or ferrite magnets.[6,7]

The magnetic hardening of the alloys is performed by heat treating within the miscibility gap after the solution treatment, producing modulated structures consisting of two phases, an FeCo rich phase (α_1) and a Cr rich phase (α_2).[11-13] Recently, Nishizawa *et al.*[14] suggested the existence of the ridge of the miscibility gap in an Fe-Cr-Co system. An equiaxial Fe-22Cr-15Co alloy, which is heat-treated within the ridge region, achieves $(BH)\max = 66.4\ \mathrm{kJ/m^3}$ (8.3 MGOe)[9] and the maximum energy products achieved with Fe-Cr-Co alloys are 91.2 $\mathrm{kJ/m^3}$ (11.4 MGOe)[10] using a ⟨100⟩ ridge single crystal Fe-22Cr-18.5Co-3Mo alloy. But small amount of α-former elements such as Ti, V, Nb, and Al, must be added in order to obtain these good magnetic properties.[4-6,12] Among these α-former elements, it is technologically known that the addition of Ti to the alloys is effective in improving the magnetic properties, especially the hysteresis loop rectangular ratio. But the metallurgical effect of Ti is not clear yet. Thus the purpose of this work is to study the metallurgical effect of Ti on the Fe-Cr-Co alloys. Two metallurgical effects of Ti can be considered as follows: (1) The carbon and nitrogen introduced from the raw materials or atmosphere are γ-forming elements, so that carbon or nitrogen contained in the alloys extends the γ-phase region. But the addition of Ti to the alloy fixes these carbon and nitrogen in forming Ti carbides or nitrides, resulting in expanding the α-phase region and improving magnetic properties. (2) The other effect is such that Ti affects the morphology of the spinodally decomposed two phases when Ti is contained within α_1 or α_2 phases.

The former effect will be confirmed by observing the Ti carbides or nitrides. The latter one is by studying the morphological changes of the two phases microstructures.



	Is / T	Br / T	Hc / kAm⁻¹	(BH)max/kJm⁻³	squarness
VO	1.54	1.48	49.2	55.2	0.73
VT(1%)	1.50	1.44	49.6	57.6	0.77
AO	1.55	1.49	44.0	48.8	0.72
AT(1.5%)	1.51	1.45	51.2	57.6	0.75

FIG. 1. Magnetic properties and demagnetization curves of VO, VT(1%), AO, and AT(1.5%) after final aging.

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TABLE I. Chemical compositions of the studied alloys.

	Fe	Cr	Co	Ti	C	N
VO	Bal.	23.92	12.32		0.010	0.009
VT(1%)	Bal.	23.68	12.04	0.84	0.018	0.008
AO	Bal.	23.80	12.17		0.009	0.031
AT(1.5%)	Bal.	24.01	12.15	0.18	0.013	0.035

II. EXPERIMENTAL PROCEDURE

The Fe-25%Cr-12%Co (in wt.%) alloys were chosen for this investigation. The alloys with or without Ti were induction melted in vacuum or in air and the amount of Ti was 1% in vacuum and 1.5% in air. The preparation of ingots were described in elsewhere.[8,9] Hereafter, the vacuum melted samples without and with Ti are designated VO, and VT (1%), and the air melted ones are designated AO, and AT(1.5%), respectively. Chemical compositions of the alloys are shown in Table I.

The alloys at first were solution-treated at 1200 °C for 1 h. After the solution treatment, the alloys were aged at 655 °C for 80 min in a magnetic field of 160 kA/m (2 kOe) and were held at 620 and 600 °C for 1 h and 2 h, respectively, followed by the controlled cooling at a rate of 5 °C/h to 500 °C and then held at 500 °C for 10 h.

The magnetic properties were measured with automatic fluxmeter. The microstructures were observed by optical microscopy, electron probe microanalysis (EPMA) and transmission electron microscopy (TEM).

III. RESULTS AND DISCUSSION

A. Magnetic properties

Figure 1 shows the magnetic properties and demagnetization curves of VO, VT(1%), AO and AT(1.5%) after final aging. The magnetic properties of VO alloy are much better than those of AO. This difference in magnetic properties is due to the content of nitrogen in the alloys. Table I shows that VO contains 0.009%N, but AO does 0.031%. The magnetic properties of vacuum melted samples, VO and VT (1%), are almost the same, but the hysteresis loop squareness of VT(1%) is slightly better than that of VO. The magnetic properties of air melted AT(1.5%) alloys are remarkably better than those of AO. Therefore, it is generally said that the Ti addition to the alloys improves magnetic properties.

B. Carbide and nitride formations

From optical microscopy and EPMA, it can be said that Ti added alloys, VT(1%) and AT(1.5%), have fine grains because of the existence of Ti compounds which suppress the grain growth.

VO alloys after the solution treatment do not show any inclusions and precipitates. But the alloy after final aging gives the precipitation along the grain boundaries surrounded by nondecomposed region of about 0.1 μm width [Figs. 2(a) and 2(b)]. Figures 2(c) and 2(d) shows the electron diffraction pattern and the diagram of the grain boundary precipitates and the precipitate is identified as $(Fe,Cr)_{23}C_6$, which has a fcc structure ($a = 1.057 - 1.064$ nm). Then it is suggested that the nondecomposed region corresponds to

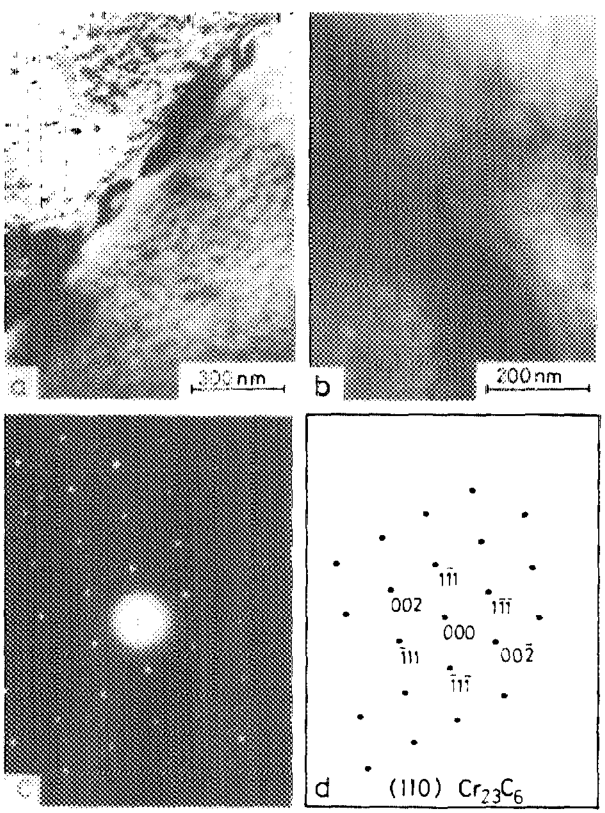

FIG. 2. (a) (b) Bright field micrographs of VO alloy after final aging, (c) electron diffraction pattern, and (d) diagram of the grain boundary precipitate in VO alloy.

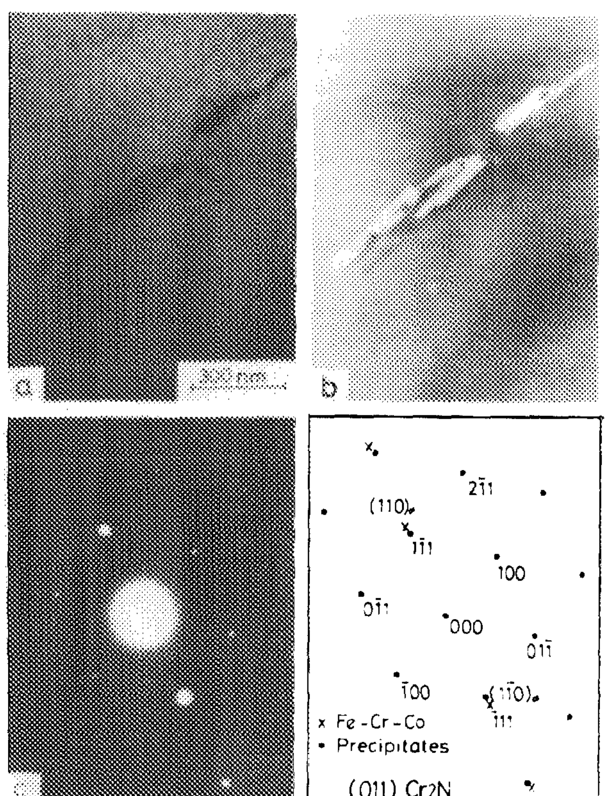

FIG. 3. (a) Bright field micrograph taken from AO alloy after final aging, (b) corresponding dark field micrograph, (c) electron diffraction pattern and (d) diagram of the precipitate inside grain.

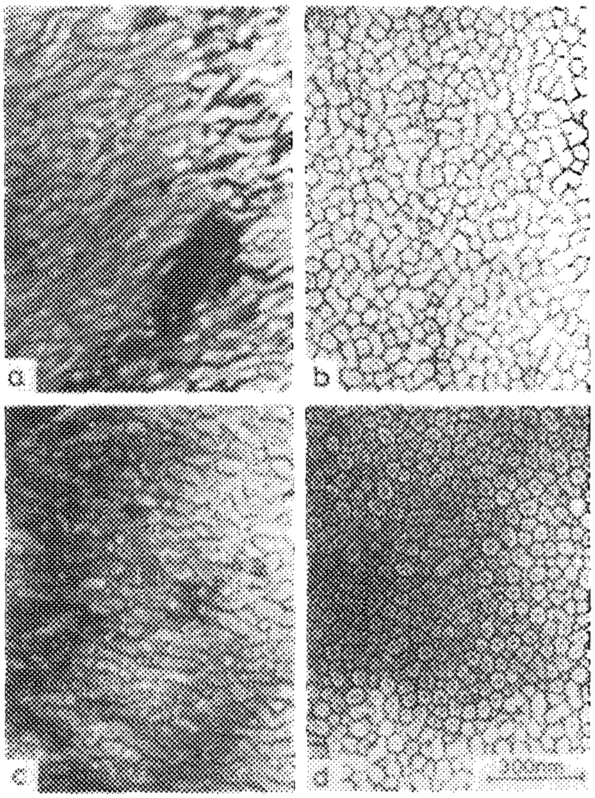

FIG. 4. Bright field micrographs taken from (a) (b) VO, (c) (d) VT(1%) alloys, and were from the area (a) (c) perpendicular and (b) (d) parallel to the direction of applied magnetic field.

the Cr-depleted zone. Because the magnetic hardening of Fe-Cr-Co alloys is associated with their spinodally decomposed phases, it can be considered that these precipitates with Cr-depleted zone deteriorate magnetic properties. But these $Cr_{23}C_6$ precipitates are not found in the VT(1%) alloys. Instead, in VT(1%) alloys, inclusions considered as TiC or TiN are present along grain boundaries and inside grains after the solution treatment. But the morphology of these inclusions of TiC and TiN remains same after final aging.

Precipitates are observed along the grain boundaries and inside grains surrounded by the nondecomposed phases in AO alloys after final aging. It can be considered that bad magnetic properties of AO alloys are due to these precipitates. The precipitates inside grains are identified as Cr_2N which has hcp structure ($a = 0.480$, $c = 0.447$ nm), as shown in Fig. 3(c). So it is understandable that the nitrogen content influences the magnetic properties. The rodlike precipitates, Cr_2N, are nearly parallel to the cubic directions. Lagneborg[15] reported that in an Fe-30% Cr alloy which contained 0.025%N, Cr_2N was precipitated along $\langle 100 \rangle \alpha$ directions in $\{100\}\alpha$ phases after 475-500 °C aging. But AT(1.5%) alloys show few $Cr_{23}C_6$ and Cr_2N, and give characteristic cuboid Ti(C,N). These Ti(C,N) could be already present in the solution treatment condition, in considering results of VT(1%) alloys. It is noticed that the addition of Ti suppressed the formation of $Cr_{23}C_6$ and Cr_2N in forming the Ti(C,N) and that the magnetic properties are improved.

C. Spinodally decomposed phases

Figure 4 shows the microstructures of VO and VT(1%) alloys after final aging. The phase with bright contrast is FeCo rich phase (α_1), and the phase with dark contrast is Cr rich phase (α_2).[3,11] No clear microstructual differences are observed in the two specimens. Air melted alloys with or without Ti show no morphological changes in the two phases microstructures. Then it can be said that 1% or 1.5% Ti addition to the alloys has little effect on morphological changes in the spinodal decomposed two phases.

As described earlier, no morphological changes of the spinodal decomposed two-phases microstructure are observed in the alloys with or without Ti. Therefore, it is suggested that the improvement of magnetic properties by adding Ti to the system is due to fixing the free carbon and nitrogen in alloys in forming the Ti carbides or nitrides.

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