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Enhancement of the thermal stability of Fe_{16}N_2 by Ti addition

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Abstract. (Fe,Ti)-N films containing the α'' -(Fe,Ti) $_{16}\text{N}_2$ phase were prepared on NaCl substrates by sputtering using facing targets. Analytical transmission electron microscopy was used for the structural studies prior to and during *in situ* annealing of the samples. Films with 3–10 at.% Ti contained the α'' -(Fe,Ti) $_{16}\text{N}_2$ and α -Fe phases at room temperature (RT). The two phases were stable during the whole process of annealing and remained unchanged when the sample was cooled to RT. The integrated electron diffraction pattern of the α'' -(Fe,Ti) $_{16}\text{N}_2$ single crystal in the [111] direction was clearly observed. This is the first report which proves that Ti doping can improve the thermal stability temperature of α'' -(Fe,Ti) $_{16}\text{N}_2$ alloy nitride to 800 °C.

1. Introduction

In recent years, Komuro *et al* [1] have grown α'' -Fe $_{16}\text{N}_2$ single-crystal films by molecular beam epitaxy and found the saturation magnetization M_s of α'' -Fe $_{16}\text{N}_2$ films to be 2.8–3.0 T at room temperature (RT). Sugita *et al* [2] have confirmed that the average magnetic moment per Fe atom in α'' -Fe $_{16}\text{N}_2$ is (3.1–3.2) μ_B . Since then, much research work has been done using iron nitrides as magnetic recording head materials. Various types of Fe–N film with both single-layer [3] and multiphase gradient films [4] have been investigated. Although the Fe–N film has a very high flux density, it has the disadvantages of high magnetostriction and poor thermal magnetic properties. The addition of the third element to form ternary Fe–M–N films (M=Ta, Zr, Hf, Nb or Ti) [5–7] has succeeded in solving the soft magnetic and thermal problems. Kopcewicz *et al* [8] studied the role of alloying elements, such as Cr, Al, Ti and Mn, in the formation and stability of the nitride phases by conversion electron Mössbauer spectroscopy. It was found that the presence of alloying elements, especially Ti, significantly extends the range of the thermal stability of α' -martensite at low N doses and γ' -Fe $_4\text{N}$ at high N doses towards higher temperatures. However, a systematic study of the thermal stability of the Fe $_{16}\text{N}_2$ phase in the ternary alloying system of (Fe, Ti)–N films has not been reported. For this reason, we prepared (Fe, Ti)–N films with a high saturation magnetization, and the purpose of this study is to explore the effect of Ti addition on the thermal stability of α'' -Fe $_{16}\text{N}_2$ by transmission electron microscopy (TEM) *in situ* annealing.

2. Experiment

The (Fe, Ti)–N films were prepared by sputtering on NaCl substrates using facing targets. The sputtering targets are composite materials consisting of 10 mm \times 4 mm Ti chips placed

on Fe (99.99%) targets of diameter 100 mm and 50 mm thickness. The sputtering gas and reactive gas were Ar (99.99%) and N_2 (99.99%), respectively. After the chamber was evacuated to a base pressure of 6×10^{-5} Pa, argon gas was introduced. During sputtering, the pressures of Ar and N_2 were kept constant at 3×10^{-1} Pa and $(3-6) \times 10^{-2}$ Pa, respectively. The substrate temperatures were maintained at 120°C . The composition of the (Fe, Ti)-N films was adjusted by varying the number of Ti chips mounted on iron targets. The deposition rate was about 0.25 nm s^{-1} . The thickness of the film was about 50 nm.

Prior to the electron microscopy examination the (Fe, Ti)-N films were floated from the NaCl substrates in distilled water and placed on Mo TEM grids. Microstructural analyses were performed with a Hitachi H-9000 300 keV high-resolution transmission electron microscope capable of energy-dispersive x-ray analysis (EDXA). The diameter of the convergent electron beam was 10 nm. During annealing, the specimen temperature was raised from RT to 800°C in increments of 50°C . The sample was held at each temperature step for 30 min before the selected-area electron diffraction (SAD) patterns and bright-field (BF) images were recorded. The cooling rate was about $10^\circ\text{C min}^{-1}$. The thickness of the film was measured by the multi-beam interference technique.

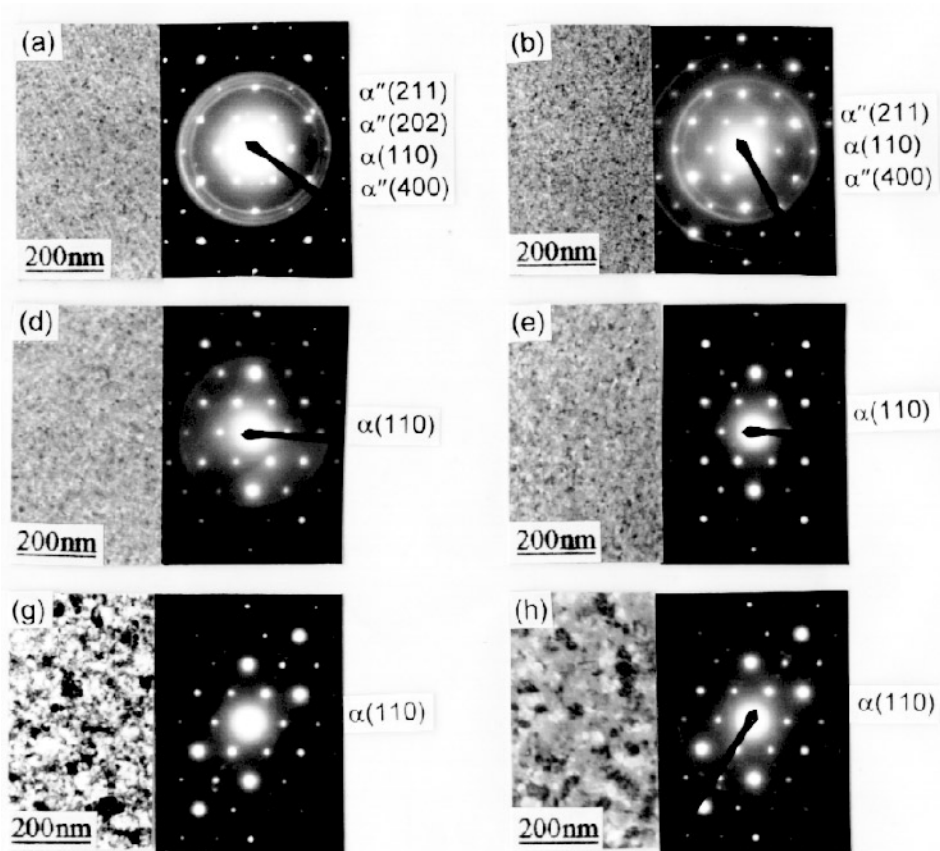


Figure 1. TEM BF images and SAD patterns of (Fe, Ti)-N films with $C_{Ti} = 3-10$ at.% deposited at $P_N = (3-6) \times 10^{-2}$ Pa and $T_s = 120^\circ\text{C}$ and *in situ* annealed at (a) RT, (b) 200°C , (c) 300°C , (d) 400°C , (e) 500°C , (f) 600°C , (g) 700°C , (h) 800°C and (I) cooled to RT. In the figure, the diffraction rings are indexed from inside to outside in turn.

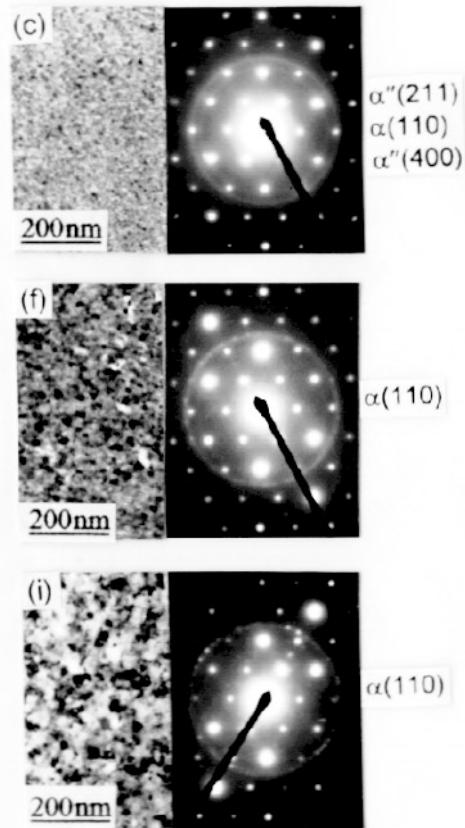


Figure 1. (Continued)

3. Results and discussion

Figure 1 shows the SAD patterns and BF images of the (Fe, Ti)-N films with the Ti concentration being $C_{Ti} = 3\text{--}10$ at.% and *in situ* annealed from RT to 800 °C followed by natural cooling to RT. In figure 1, all the SAD patterns contain single-crystal diffraction spots, and the spots display a quasi-sixfold symmetry. This pattern is the stereographic projection in the $[\bar{1}11]$ direction of single-crystal α'' phase, as indexed in Figure 2. EDX was made of the same area of the SAD to verify the composition of the area in the film used for SAD. The composition of the area used for SAD was determined to be $C_{Fe} = 80\text{--}85$ at.%, $C_{Ti} = 3\text{--}10$ at.% and $C_N = 7\text{--}10$ at.%. There are no diffraction spots or rings of Ti or TiN and iron-titanium solid solution or compound in all the SAD patterns. Therefore the phase corresponding to the single-crystal spots of the SAD was determined to be a Ti-containing 16:2 nitride, which can be denoted by $\alpha''\text{-(Fe, Ti)}_{16}N_2$. In the as-deposited film, it consists of $\alpha''\text{-(Fe, Ti)}_{16}N_2$ single-crystal diffraction spots and polycrystalline diffraction rings. The rings are due to the diffraction of $\alpha\text{-Fe}$ and $\alpha''\text{-(Fe, Ti)}_{16}N_2$, as given in figure 1(a). The sample showed no structural changes when annealed at 200 °C. When the sample was heated to 400 °C, the intensity of the diffraction rings became weaker than before. The sample showed no structural changes when annealed at temperatures ranging between 400 and 800 °C. $\alpha''\text{-(Fe, Ti)}_{16}N_2$ and $\alpha\text{-Fe}$ phases coexisted in the microstructure and they were

thermally stable during annealing.

According to the experiments by Jack [9] and Kim and Takahashi [10], the $\alpha''\text{-Fe}_{16}\text{N}_2$ phase is metastable and it decomposes into $\alpha + \gamma'$ phases at around 200–300 °C. Sugita *et al* [2] claimed that the $\alpha''\text{-Fe}_{16}\text{N}_2$ crystal is stable at 400 °C while, beyond 400 °C, $\alpha''\text{-Fe}_{16}\text{N}_2$ dissolves into Fe and Fe_4N . In our study, we observed repeatedly that the $\alpha''\text{-(Fe, Ti)}_{16}\text{N}_2$ single crystal is thermally stable when *in situ* annealed from RT to 800 °C. This better stability of the Ti-containing α'' phase may be caused by the effect of Ti addition.

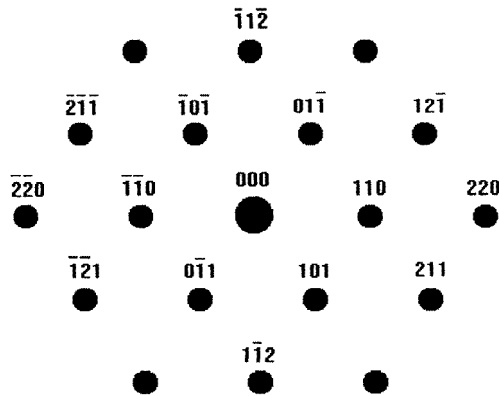


Figure 2. The illustration of the electron diffraction pattern corresponding to figure 1 of single-crystal α'' with $[111]$ incidence.

In order to determine accurate lattice constants a and c of the $\alpha''\text{-(Fe, Ti)}_{16}\text{N}_2$ phase, the lattice constants a and c calculated from each plane are plotted against the Nelson–Riley function $(\cos^2 \theta)/(\sin \theta) + (\cos^2 \theta)/\theta$ in figure 3. The extrapolated value of the lattice constants $a = 0.613$ nm and $c = 0.632$ nm of the $\alpha''\text{-(Fe, Ti)}_{16}\text{N}_2$ phase are somewhat larger than those of the $\alpha''\text{-Fe}_{16}\text{N}_2$ precipitates in bulk powder reported by Jack [9]; so the interstitial sites are wider in the Fe–Ti lattice than in the Fe lattice, suggesting that some Fe atom positions are occupied by Ti atoms. The 16:2 nitride is considered to be a nitrogen ordered form of the tetragonal Fe–N solid solution, which is derived without changing the basic arrangement of Fe atoms in the BCC structure. Therefore, it can be speculated that the Ti-containing 16:2 nitride also forms with less strain energy, leading to a higher stability. The grain size as observed from the BF images can be seen to increase progressively from 10–15 nm at RT to 80–100 nm at 800 °C, and subsequent cooling to RT. The magnetic properties were measured with a VSM for the as-deposited film and the annealed film when cooled to RT. The as-deposited film exhibits a high saturation magnetization M_s up to 2.6 ± 0.08 T, and the annealed film has $M_s = 2.56 \pm 0.04$ T. This confirms the high M_s of the $\alpha''\text{-(Fe, Ti)}_{16}\text{N}_2$ phase.

4. Summary

We have newly found that Ti addition can enhance the thermal stability of the 16:2 nitride. The as-deposited film with 3–10 at.% Ti contains $\alpha\text{-Fe}$ and $\alpha''\text{-(Fe, Ti)}_{16}\text{N}_2$ phases. The two phases exist stably during the whole annealing process, and remain stable when the sample is cooled to RT. It is suggested that appropriate Ti addition may stabilize the $\alpha''\text{-(Fe, Ti)}_{16}\text{N}_2$ phase to a temperature of 800 °C. The integrated electron diffraction pattern

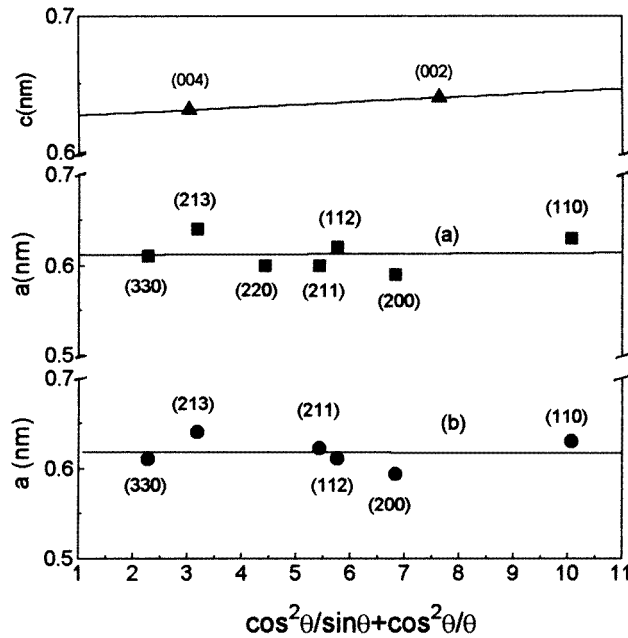


Figure 3. Extrapolation of the lattice constant of α'' phase in (Fe, Ti)-N films against the Nelson-Riley function. The films were deposited at $P_N = (3-6) \times 10^{-2}$ Pa and $T_s = 120^\circ\text{C}$ (a) $C_{Ti} = 5$ at.% and (b) $C_{Ti} = 10$ at.%.

of the α'' -(Fe, Ti) $_{16}$ N $_2$ single crystal in the $[\bar{1}11]$ direction has been observed distinctly for the first time. The mechanism of the higher thermal stability of α'' -(Fe, Ti) $_{16}$ N $_2$ is not clear and needs exploring thoroughly.

Acknowledgments

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