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Effects of B addition on the microstructure and magnetic properties of Fe-Co-Mo alloys

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The microstructure, precipitation hardening and magnetic properties of melt-spun $Fe_{78}Co_{11}Mo_{11}$ and $Fe_{74}Co_{11}Mo_{11}B_4$ alloys were studied. It is shown that B addition increases the precipitation reaction temperature of the supersaturated matrix from 605 °C for the $Fe_{78}Co_{11}Mo_{11}$ alloy to 640 °C for the $Fe_{74}Co_{11}Mo_{11}B_4$ alloy. In the $Fe_{78}Co_{11}Mo_{11}$ alloy, a cotton-shaped $(Fe,Co)_7Mo_6$ precipitate is observed inside the grains of the matrix phase. In the $Fe_{74}Co_{11}Mo_{11}B_4$ alloy, in addition to the $(Fe,Co)_7Mo_6$ phase, spherical MoB_2 precipitates are also observed. Compared to the $Fe_{78}Co_{11}Mo_{11}$ sample, the $Fe_{74}Co_{11}Mo_{11}B_4$ sample exhibits a finer and more homogeneous microstructure with more equiaxed grains. This finer microstructure explains the enhanced hard magnetic properties in the $Fe_{74}Co_{11}Mo_{11}B_4$ sample ($M_r = 60.4$ A m^2/kg, $_iH_c = 20.8$ kA/m) compared to those of the $Fe_{78}Co_{11}Mo_{11}$ sample ($M_r = 56.5$ A m^2/kg, $_iH_c = 17.3$ kA/m). Furthermore, the $Fe_{74}Co_{11}Mo_{11}B_4$ sample shows better antioxidant ability than the $Fe_{78}Co_{11}Mo_{11}$ sample, especially when the temperature exceeds 400 °C.

1. Introduction

Nearly all high performance permanent magnets contain rare-earth elements. Problems with supply constraints and high prices of rare-earth elements necessitate the development of new non-rare-earth-containing permanent magnet materials. The Fe-Co-Mo alloy is a potential candidate material for permanent magnets with high saturation magnetization and good mechanical properties. This alloy is soft in the solutionized state, but tempering treatments can increase the hardness to the range of classic high-speed steels [1–3]. Previous studies showed that the strengthening is caused by the precipitation of the nanometer-sized intermetallic μ phase formed from a supersaturated matrix [4,5]. The μ phase has a mixed chemical composition $(Fe,Co)_7Mo_6$. Understanding of the microstructure-property relationships is vital for the improvement of the Fe-Co-Mo alloys. The type, size and distribution of the precipitates can influence the hard magnetic properties of the alloys. However, to date, most studies on the Fe-Co-Mo alloys have been focused on the relationship between the microstructure and mechanical properties [6–9]. To the best of our knowledge, to date, there have been no investigations regarding the effects of the precipitates on the magnetic properties of Fe-Co-Mo alloys.

Alloys with a cubic structure usually do not show high magnetocrystalline anisotropy, which is necessary to obtain a high coercivity of permanent magnets [10]. In Nd-Fe alloys, the addition of B is helpful in forming the tetragonal structure $Nd_2Fe_{14}B$ [11] with a c/a ratio of 1.38, leading to hard magnetic properties. Furthermore, B addition can enhance the glass-forming ability and can reduce the grain size of the Fe-based alloys [12,13]. It is important to study whether B addition can produce a new crystal structure type and can improve the hard magnetic properties of the Fe-Co-Mo alloys.

In this paper, the effects of B addition on the microstructure and magnetic properties of Fe-Co-Mo alloys have been investigated. The correlations among the microstructure, the precipitation behavior and the magnetic properties are established and discussed.

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2. Experiment

Alloy ingots with the nominal compositions of $Fe_{78}Co_{11}Mo_{11}$ and $Fe_{74}Co_{11}Mo_{11}B_4$ were prepared by arc-melting under purified argon atmosphere. The ingots were remelted four times to ensure their homogeneity. The arc-melted ingots were cut into small pieces for melt-spinning. Alloy ribbons were obtained by melt-spinning the ingot pieces from a quartz tube with an ~0.6 mm orifice under argon atmosphere using a wheel speed of 43 m/s. The ribbon samples were isothermally annealed at 600–800 °C for 30 min in sealed quartz tubes under Ar and were then quenched to room temperature in water. The magnetic properties were measured using a vibrating sample magnetometer (VSM, Quantum Versalab) with a maximum magnetic field of 3 T. X-ray diffraction (XRD, Rigaku Ultima IV) with Cu K_α radiation was used to identify the phases present in the samples. The XRD were performed using continuous scanning, with a rate of 0.5°/min and a step size of 0.05°. The thermal phase transitions of the as-spun ribbons were traced using a differential thermal analysis (DTA, Diamond Perkin-Elmer) instrument at a heating rate of 10 °C/min under Ar flow. The microstructure of the samples was characterized by scanning electron microscopy (SEM, JEOL JSM-6330F) and transmission electron microscopy (TEM, JEOL JEM-3010). The SEM samples were etched in a nitric acid (5 vol%)+alcohol (95 vol%) solution for 8–10 s; then, the samples were cleaned with deionized water. The TEM samples were prepared by mechanical grinding and by ion-milling the ribbons from both sides. The oxidation resistance of the ribbons was evaluated by the oxidation weight gain experiment performed in air atmosphere using a thermogravimetric analyzer (TGA, Diamond Perkin-Elmer) with a heating rate of 10 °C/min. The experimental parameters are listed in Table 1.

3. Results and discussion

Fig. 1 shows the dependence of the saturation magnetization M_s, the intrinsic coercivity $_iH_c$ and the remanence M_r on the annealing temperature for the $Fe_{78}Co_{11}Mo_{11}$ and $Fe_{74}Co_{11}Mo_{11}B_4$ ribbons. The detailed data are listed in Table 2. It can be seen that, for both alloys, the M_s decreases monotonically with increasing annealing temperature. The as-spun ribbons exhibit the highest saturation magnetization. In contrast, for both alloys, the $_iH_c$ and M_r first increase with increasing annealing temperature, reach maximum values at an optimum temperature and then decrease with the further increase in the annealing temperature. For the $Fe_{78}Co_{11}Mo_{11}$ sample, the optimum temperature is 700 °C, while for the $Fe_{74}Co_{11}Mo_{11}B_4$ sample, the optimum temperature is 750 °C.

Fig. 2 shows the hysteresis loops of the $Fe_{78}Co_{11}Mo_{11}$ and $Fe_{74}Co_{11}Mo_{11}B_4$ ribbons before and after annealing at their optimum temperatures. For the $Fe_{78}Co_{11}Mo_{11}$ sample, $_iH_c$ increases from 0.9 kA/m to 17.3 kA/m, and the M_r increases from 12.5 A m^2/kg to 56.5 A m^2/kg. For the $Fe_{74}Co_{11}Mo_{11}B_4$ sample, the $_iH_c$ increases

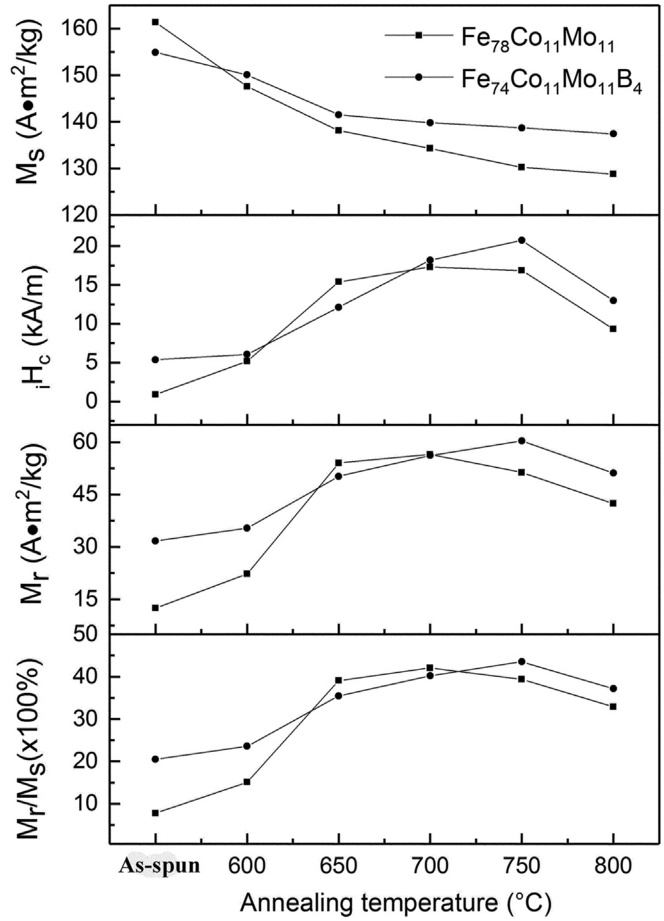

Fig. 1. Magnetic properties (M_s, $_iH_c$, M_r and M_r/M_s) of the $Fe_{78}Co_{11}Mo_{11}$ and $Fe_{74}Co_{11}Mo_{11}B_4$ ribbons before and after annealing at various temperatures for 30 min.

from 5.3 kA/m to 20.8 kA/m, and the M_r increases from 31.7 A m^2/kg to 60.4 A m^2/kg. The $Fe_{74}Co_{11}Mo_{11}B_4$ ribbons exhibit better hard magnetic properties than the $Fe_{78}Co_{11}Mo_{11}$ ribbons. This result means that the addition of B is helpful for enhancing the hard magnetic properties of the Fe-Co-Mo alloy. The M_r and $_iH_c$ values of $Fe_{74}Co_{11}Mo_{11}B_4$ annealed at optimum temperature are very close to those of the commercial ferrite magnets (M_r = 14–55 A m^2/kg, $_iH_c$ = 50–160 kA/m) and the commercial Alnico magnets (M_r = 61–147 A m^2/kg, $_iH_c$ = 38–148 kA/m) [14,15]. One can expect better magnetic properties in the Fe-Co-Mo-B alloys by further optimizing the composition and the experimental procedure.

Fig. 3 shows the XRD patterns of the as-spun $Fe_{78}Co_{11}Mo_{11}$ and $Fe_{74}Co_{11}Mo_{11}B_4$ ribbons. It is found that the ribbons consist of a dominant body-centered cubic phase, which is an α-Fe(Co,Mo)

Table 1
A list of the experimental parameters.

Experimental name	Experimental parameters
Arc-melting	remelted the ingot 4 times, argon atmosphere
Melt-spinning	wheel speed 45 m/s, an orifice diameter ~0.6 mm for quartz tube, argon atmosphere
Annealing	600–800 °C for 30 min, argon atmosphere
VSM	maximum magnetic field 3 T
XRD	Cu K_α radiation, continuous scanning, speed 0.5°/min, step size 0.05°, generator voltage 40 kV, tube current 40 mA
SEM	etched the ribbons in nitric acid (5 vol%)+alcohol (95 vol%) solution for 8–10 s
TEM	mechanically ground and ion-milled the ribbons from both sides
DTA	heating rate 10 °C/min, argon atmosphere
TGA	heating rate 10 °C/min, air atmosphere