Research on Preparation of Sm-Fe-N Anisotropic Magnetic Powder by Nitriding Melt-Spun Sm_2Fe_{17} Fine Columnar Crystals

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Abstract. The Sm_2Fe_{17} fine columnar crystals ribbon was obtained by melt-spinning at 6m/s surface rotating velocity of Cu wheel and in suitable thickness of ribbon. Preparation process of its nitride powder was primarily explored by means of XRD, SEM and the measurement of magnetic properties. The columnar crystal texture of Sm_2Fe_{17} in the ribbon is very beneficial to increase magnetic anisotropy of its nitride Sm-Fe-N powder prepared through powder metallurgy process.

Introduction

$Sm_2Fe_{17}N_x$ (X≤3) has excellent intrinsic magnetic properties and some methods such as mechanical alloying (MA), hydrogen decrepitation (HDDR), and reduction diffusion (R/D), rapid quenching (RQ) and powder metallurgy (PM) have been developed to produce $Sm_2Fe_{17}N_x$ powders since the discovery of $Sm_2Fe_{17}N_x$ in 1990 [1-5]. Anisotropic $Sm_2Fe_{17}N_x$ materials may have much higher $(BH)_{max}$ as compared to that of corresponding isotropic materials. Therefore, it is of great interest to prepare anisotropic materials. Up to now, PM process has been widely reported to be successfully applied to make anisotropic $Sm_2Fe_{17}N_x$ magnetic powder. Towards the Sm-Fe alloy obtained by conventional ingot melting technique, it needs diffusion annealing for dozens of hours at a high temperature above 1000°C in order to obtain the single phase Sm_2Fe_{17} compound. If Sm-Fe alloy was obtained by strip casting technique, the annealing time might be shortened [4]. Those annealed Sm-Fe alloys have large Sm_2Fe_{17} equiaxed grain sizes. They undergo pulverization, nitrogenization and fine grinding, resulting in the formation of anisotropic $Sm_2Fe_{17}N_x$ powders. But their demagnetization curves have poor squarenesses. One reason for this is that some Sm-Fe-N particles contain grain boundaries and thus do not belong to singe-domain particles. Although Sm_2Fe_{17} grain sizes in the annealed alloy are larger than the diameter of single-domain particles of $Sm_2Fe_{17}N_x$, it is difficult to guarantee all fracture paths along grain boundaries during the preparation of the nitride powder. In order to improve the anisotropic magnetic properties, we explored preparation of Sm-Fe-N anisotropic magnetic powder by nitriding melt-spun Sm_2Fe_{17} fine columnar crystals, which almost have uniform grain orientation.

Experimental Procedure

Firstly, Sm-Fe ingot was prepared by vacuum induction melting with high purity Sm(99.9%) and Fe (99.9%) as raw materials and casting in a water cooled copper mould. An extra 30 wt% Sm compared to the nominal composition of Sm_2Fe_{17} was added to compensate the evaporation of the Sm. Then, the ingot was crushed and used to produce Sm-Fe ribbons in a melt-spinning machine in argon atmosphere. The ribbons with different thicknesses were obtained by controlling rotating velocity of Cu roller with diameter of 0.22 m. They were then annealed and mechanically pulverized. Nitrogenization was

executed at 490°C for 5.5 hour with a nitrogen pressure of 100 kPa followed by evacuating for 1.5 hour. The nitride powder was further finely ground by high energy ball milling with 36:1 weight ratio of ball to the power in petroleum ether. The samples were fabricated by mixing Sm-Fe-N powders with epoxy resin and then aligned in a magnetic field of 15 kOe. Their magnetic properties were measured using a vibrating sample magnetometer (VSM) and present with no demagnetization correction and usage of a density of 7.8 g/cm^3. X-ray diffraction (XRD) and scanning electronic microscopy (SEM) was performed to study the microstructures.

Results and Discussion

We tested 450-800 turns per minute of the rotating copper roller to make the ribbons and found that there are columnar crystals growing from fine equiaxed grains near the copper roller. When the rotation rate is 500 turns/min (i.e. 6m/s linear velocity), the strip distinctly possesses a high proportion of columnar crystals texture. Fig.1 shows the columnar crystals texture and its cross-section. With the increase of the rotation rate, cooling rate increases, so that equiaxed grains zone increase and the corresponding columnar crystals zone decrease. Fig.2 is XRD charts of the side adjacent to the roller and free side of the strip. Rapid solidification by melt spinning was found to promote structural disorder, leading to the formation of the $SmFe_7$ ($TbCu_7$-type) structure besides the Sm_2Fe_{17} (Th_2Zn_{17}-type) equilibrium structure [1-3]. The difference between the two structures is that the transition metal dumbbells possess long-range order in the Sm_2Fe_{17} structure, whereas in the $SmFe_7$ structure they randomly occupy Sm sites. The resulting structural relationships between the two structures are $a_{2\text{-}17}=3^{1/2}a_{1\text{-}7}$ and $c_{2\text{-}17}=3c_{1\text{-}7}$. Their XRD configurations are analogous. The Sm_2Fe_{17} structure is distinguishable from the $SmFe_7$ structure by the presence of superlattice peaks such as {006} and {024} [1-3]. Fig.2 (a) indicates that Sm_2Fe_{17} phase exists in the fine equiaxed grain zone as appearance of the peaks of (006) and (024). The disappearance of the many peaks in Fig.2 (b), including (006) and (024), indicates the existence of preferential growth of Sm_2Fe_{17} columnar crystals. Combined Fig. 1 and Fig. 2, it can be concluded that the phases in colors of grey and white in Fig. 1 should be of Sm_2Fe_{17} and $SmFe_3$ respectively. Meanwhile, we cannot exclude the existence of $SmFe_7$ structure, since the many peaks of $SmFe_7$ XRD chart are much close to the location of the some peaks of Sm_2Fe_{17} XRD chart.

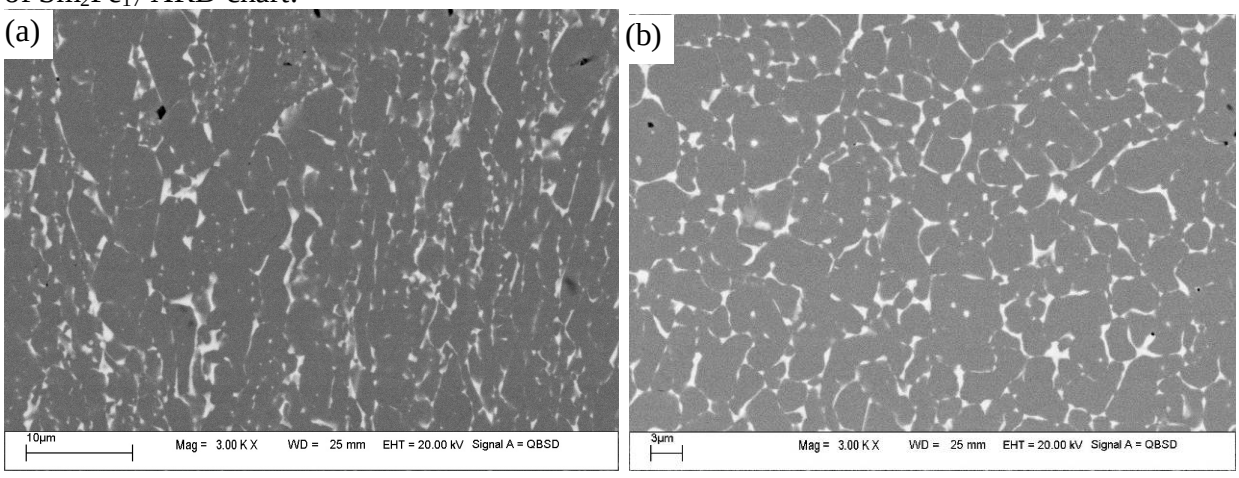

Fig.1 The microstructures of Sm_2Fe_{17} columnar crystals: (a) Longitudinal direction; (b) Cross-section.

The Sm-Fe-N powder has better magnetic properties when its corresponding Sm_2Fe_{17} columnar powder is treated at a high temperature before nitrogenization, as listed in table 1. The powder was made by treating -300 mesh crushed Sm_2Fe_{17} columnar powders at 700°C for different holding time in vacuum atmosphere, then nitridation and high-energy ball milling at rotating rate of 270n/min for 2 hours. The reason for the above should be that the treatment transforms some $SmFe_7$ phase (its nitride $SmFe_7Nx$ is a soft magnetic phase) into Sm_2Fe_{17} and eliminate some crystal lattice imperfections.

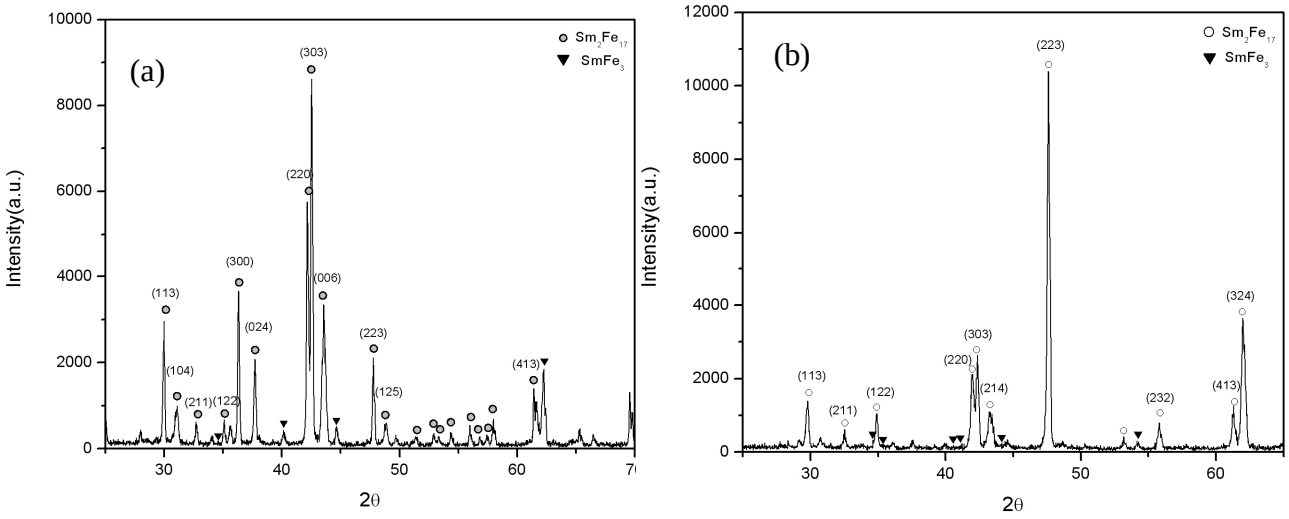

Fig.2 XRD charts of melt-spun Sm-Fe strip: (a) the side adjacent to the roller; (b) free side

Table 1 Effects of the heat treatment before nitrogenization on the properties of bonded Sm-Fe-N magnets.

Sample number	Holding time at 700°C	B_r/T	H_{ci} / Oe	$(BH)_{max}$/kG·Oe
#1	0 minute	0.2801	463	270
#2	10 minutes	0.3104	545	349
#3	1 hour	0.5699	1438	1641
#4	2 hours	0.6720	2104	3331

Fig 3 (a) and (b) are the magnetic hysteresis loops of magnetic field aligned and non –aligned Sm-Fe-N samples. It can be found that the aligned magnetic field make the remanence of the sample distinctly increases from 0.3780T to 0.6400T, which displays that the Sm-Fe-N powder has a good magnetic anisotropy. This is attributed to that the Sm-Fe columnar crystals have coincident orientation; therefore, even though the fractures did not take place along boundaries during milling, the grains in Sm-Fe-N polycrystalline particle should have an accordant orientation.

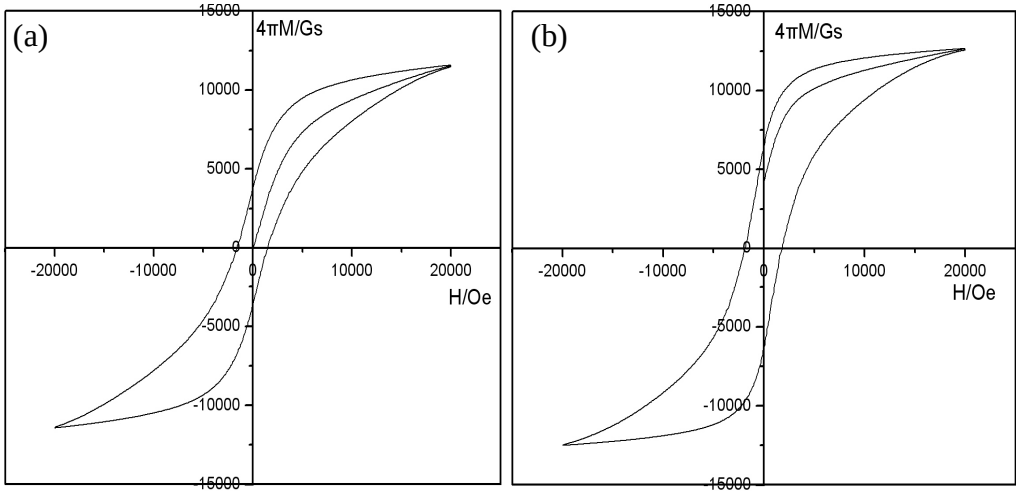

Fig.3 The magnetic hysteresis loops of bonded Sm-Fe-N samples non –aligned (a) and aligned (b) by magnetic field

Fig. 4(a) and Fig. 4(b) are the SEM images of Sm-Fe-N powders ball-milled for 1 hour and 2 hour. When ball milling time is 1 hour, a majority of the powder appears in sliver shape (Fig. 4(a)), indicating fractures take place along rich-samarium phase between Sm_2Fe_{17} columnar crystals. But the powder

have low coercivity and remanence as its particle sizes are much bigger than Sm-Fe-N single-domain size which was estimated to be about 0.3μm [1, 4]. With the balling time increasing to 2 hours, the particle sizes of the powder reduce to 1-2μm (seen Fig. 4(b)) and its magnetic properties further increase to those of sample 4# in table 1. On this basis, if the rotation rate of the ball-milling equipment upgrades from 270 to 400n/min, the magnetic properties will go down owing to oxidation, though the particle sizes further decrease.

The obtained Sm-Fe-N powder was analyzed by XRD and α-Fe was found. The α-Fe should come from oxidation of Sm-Fe and Sm-Fe-N or the reaction of $SmFe_3$ and $SmFe_7$ with N_2 during processing. Demagnetization of Sm-Fe-N is controlled by nucleation process of reversed domain[1, 5], which can easily be generated near all types of defects regions or a soft magnetic phase, such as many tiny pores existed in Sm-Fe melt-spun strip, above-mentioned α-Fe and $SmFe_7Nx$ nitride of $SmFe_7$ which does not fully convert into Sm_2Fe_{17} during annealing. If some measures are taken to eliminate crystal lattice imperfections, pores, α-Fe, $SmFe_7N_x$ and oxidation, anisotropic magnetic properties of the Sm-Fe-N powder will acquire broad space for increase.

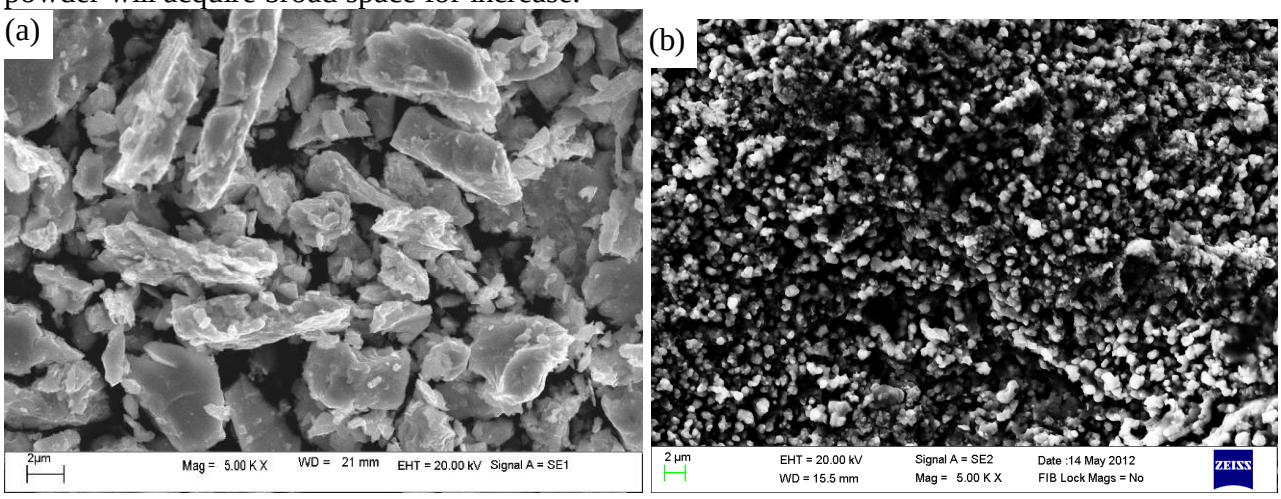

Fig. 4 SEM images of Sm-Fe-N powders ball-milled for 1 hour (a) and 2 hour (b)

Summary

Sm_2Fe_{17} columnar crystals alloy can be made by controlling cooling rate and thickness of Sm-Fe melt spun ribbon. The Sm-Fe-N powder prepared by PM process using the alloy has high magnetic anisotropy; the remanence of its anisotropic bonded magnet enhances 1 time compared with that of its isotropic bonded magnet. This lays out extensive prospect. Meanwhile, it also leave many problem to solved, such as decreasing the other phase except Sm_2Fe_{17} phase and infects in annealed Sm-Fe alloy, avoiding oxidation during processing.

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