Magnetic Properties of α -Fe-Nd(Fe, TM)₁₂N_x Exchange Spring Magnets Synthesized by Mechanical Alloying

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SYNOPSIS

The usefulness of a permanent magnet depends on its energy product $(BH)_{\max}$ and it is desirable to increase both the coercivity and remanence. Mechanical alloying with its inherent advantage of grain refinement is expected to result in enhanced coercivity. The advantage of grain size refinement by mechanical alloying is fully utilized, if this can lead to remanence enhancement at the same time. Such a thing is possible if nano scale mixture of exchange coupled hard and soft phases are produced. A magnet with such a two phase mixture is called exchange spring magnet. In the present study exchange spring magnets of α -Fe-Nd(Fe,TM)₁₂N_x (where TM = V, Mo) are synthesized by mechanical alloying and a two stage heat treatment. The effect of nitrogenation condition on the magnetic properties has been studied. The optimum nitrogenation temperature was found to be 673 K. Exchange spring magnet of α -Fe-Nd(Fe,Mo)₁₂N_x showed a maximum energy product of 48 kJ/m³ and a spring back of 50%.

KEY WORDS

mechanical alloying, exchange spring magnet, coercivity, remanence.

1 Introduction

The suitability of the mechanical alloying technique for the synthesis of permanent magnets has been demonstrated by the pioneering work of Schultz and co-workers¹⁻⁵. As the usefulness of a permanent magnet depends on its energy product $(BH)_{\max}$, it is desirable to increase both the coercivity and remanence. Mechanical alloying with its inherent advantage of grain refinement is expected to result in enhanced coercivity. At the same time, efforts to enhance the remanence of these isotropic permanent magnets led to the development of exchange spring magnets⁶⁻¹⁰. Exchange spring magnets are a new class of permanent magnets with exchange coupled hard and soft phases. The hysteresis loop is characteristic of a single phase material, even though magnetically two distinct phases are present. The soft phase contributes to the enhanced remanence and the hard phase to the

coercivity. As α -Fe has the highest magnetic moment per atom, it is logical that one tries to synthesize exchange spring magnets with α -Fe as the soft phase and a good hard magnetic phase. Rare earth transition metal compounds with 2:17 structure (Th₂Zn₁₇ type or Th₂Ni₁₇ type) or 1:12 structure (ThMn₁₂ type) are found to exhibit good hard magnetic properties¹¹⁻¹⁴. The limitations imposed by the low Curie temperature (T_c) could be overcome by introducing interstitial nitrogen or carbon¹⁵⁻¹⁸. It is interesting to mention here that the interstitially nitrided or carburized 2:17 phase with Sm shows uniaxial anisotropy, whereas, interstitially nitrided or carburized 1:12 with Nd shows uniaxial anisotropy. As Nd is cheaper than Sm it is desirable to produce exchange spring magnets with Nd rather than Sm. A comparison between the 1:12 and 2:17 phases is shown in Table 1. Though a number of studies has been carried out on the exchange spring

magnets with 2:17 as the hard phase^{9,10,19)}, the possibility of exchange spring magnets with 1:12 as the hard phase has been overlooked. In the present article we report the results on the synthesis and magnetic properties of the hitherto unexplored exchange spring magnets of α -Fe-Nd(Fe,TM)₁₂N_x, where TM = V and Mo.

Table 1 : Comparison of 1:12 and 2:17 hard phases

Advantages of 1:12 over 2:17	
1. Nd is cheaper than Sm	
2. Theoretical estimation of maximum energy product	
2:17	3975 kJ/m ³
1:12	4373 kJ/m ³
3. Easy magnetization direction at room temperature	
Sm ₂ Fe ₁₇	ab plane
Nd(Fe,TM) ₁₂	C-axis
Sm ₂ Fe ₁₇ N _x	C-axis
Nd(Fe,TM) ₁₂ N _x	C-axis
Sm ₂ Fe ₁₇ Cx	C-axis
Nd(Fe,TM) ₁₂ Cx	C-axis
4. Magnetocrystalline anisotropy constant	
KSm ₂ Fe ₁₇ N ₃	= 8 MJ/m ³
KNd(Fe,Mo) ₁₂ N _x	= 9 MJ/m ³
Disadvantages of 1:12 over 2:17	
1. Nd-Fe Binary 1:12 compound does not exist.	
2. The enhancement in T _c is less for 1:12 than 2:17 upon nitrogenation	

2 Experimental procedure

Elemental powders of Fe, Nd, V and Mo with more than 99.9% purity were used. Elemental powder mixtures of nominal composition were taken in a stainless steel vial (SUS 304) with balls of the same material having a diameter of 9.6 mm. The vial containing balls and powder in the ratio of 100:1 respectively were milled at a milling speed of 95 rpm. The total weight of powder was 36 g and the samples were milled for 360 ks. The sealing of the vial and its opening

after the completion of milling was carried out in a glove box maintained under argon atmosphere with oxygen content less than 1 ppm. The milled powders were taken in a quartz tube and a two stage heat treatment of annealing and nitriding was carried out to produce a mixture of two phase and the nitride of the hard phase respectively. The as milled, annealed and nitrided powders were characterized by X-ray diffraction. The effect of nitrogenation temperature was studied. The magnetic properties of the nitrided samples were measured in a vibrating sample magnetometer operated with a maximum field strength of 1200 kAm⁻¹ (15 kOe). The magnetization of the nitrogenated powder was calculated assuming the full density of 7.5 Mg/m³. The correction for demagnetization fields was performed using the demagnetization factor N = 0.18 obtained from the demagnetization curve of Ni powder measured by the same method.

Fig.1 X-ray diffraction patterns of Nd₉Fe₈₀V₁₁ alloy mechanically alloyed, annealed and nitrogenated at two different temperatures.

3 Results and discussion

3.1 Nd-Fe-V system

Fig.1 shows the X-ray diffraction patterns of Nd₉Fe₈₀V₁₁ alloy mechanically alloyed, annealed and nitrided at two different temperatures. The as milled sample shows a mixture of an amorphous phase and α -Fe. Upon annealing at 1073 K for 1.8 ks a mixture of Nd(Fe,V)₁₂ and α -Fe has formed. After nitrogenation the shift in the Nd(Fe,V)₁₂ peaks can be clearly observed. Fig.2 shows the hysteresis loop of the alloy nitrogenated at 723 K for 7.2 ks. The observed remanence, coercivity and the maximum energy product are also indicated. Though the X-ray diffraction patterns indicate a small volume fraction of α -Fe, the observed coercivity is very less. Earlier study²⁰⁾ has shown that the coercivity increases significantly when nitrided under a reduced atmosphere (N₂+H₂) than pure N₂. This may help in preventing the adverse effects due to oxygen. As no oxygen analysis has been carried out during the present study, it is not possible to rationalise the causes for the observed properties. Further studies are required to improve the magnetic properties.

Fig.2 Hysteresis loop of Nd₉Fe₈₀V₁₁ alloy nitrogenated at 723 K for 7.2 ks. The observed magnetic properties are also indicated.

3.2 Nd-Fe-Mo system

A number of alloys has been tried in this system as 1:12 compound readily forms in the presence of Mo. Also, Mo is less prone to oxidation compared to V. Fig.3 shows X-ray diffraction patterns of a number of alloys studied. It is clearly seen that the volume fraction of 1:12 phase is not considerable in the first two alloys, namely, Nd_{5.5}Fe₈₈Mo_{6.5} and Nd₉Fe₈₅Mo₆. The volume fraction of 1:12 is appreciable in the other three alloy systems. Hence, the hysteresis loops of these three alloys are compared in Fig.4. In accordance with the observed X-ray diffraction patterns, Nd₉Fe₈₂Mo₉ with a low volume fraction of Nd(Fe,Mo)₁₂N_x shows the smallest coercivity, whereas, the Nd₉Fe₈₀Mo₁₁ which is nearly a single Nd(Fe,Mo)₁₂N_x phase shows the highest coercivity. Nd_{9.7}Fe₈₄Mo_{6.3} with comparable volume fraction of Nd(Fe,Mo)₁₂N_x and α -Fe shows the optimum properties. It is interesting to note that the hysteresis loop of this alloy shows the characteristic features of a single

Fig.3 X-ray diffraction patterns of various Nd-Fe-Mo alloys mechanically alloyed and annealed at 1073 K for 1.8 ks in vacuum. The nitrogenation conditions are as indicated.

phase material, though indeed it contains a mixture of two phases. The maximum energy product observed in this alloy is 48 kJ/m^3 . The alloy also exhibits a reasonable spring back as shown in Fig.4 indicating a good coupling between the hard and the soft phases. The magnetic properties of all the alloys studied are listed in Table 2.

The effect of nitrogenation condition on the magnetic properties has been studied. Fig.5 shows the X-ray diffraction patterns of the alloys nitrided at different temperatures. It can be clearly seen that at higher nitriding temperatures the volume fraction of the hard phase, $\text{Nd}(\text{Fe},\text{Mo})_{12}\text{N}_x$, decreases and the volume fraction of $\alpha\text{-Fe}$ increases. The consequent effect on magnetic properties is clearly reflected in Fig.6. With increasing

nitrogenation temperature the coercivity increases initially up to 673 K and decreases afterwards. At the same time remanence increases with increasing nitrogenation temperature up to 723 K and decreases afterwards. The maximum energy product $(\text{BH})_{\text{max}}$ as a function of nitrogenation temperature is shown in Fig.7. The highest energy is observed in the sample nitrogenated at 673 K for 7.2 ks. This is because up to this temperature both the coercivity and remanence increase. However, beyond 673 K, $(\text{BH})_{\text{max}}$ is found to decrease even though there is remanence enhancement. This is because of the large decrease in coercivity. The total variation in remanence is only 8% compared to 60% variation in coercivity. The steep fall in $(\text{BH})_{\text{max}}$ beyond 723 K can be attributed to the decrease in both coercivity and remanence.

Fig.4 Comparison between the hysteresis loops of the three different alloys of Nd-Fe-Mo. $\text{Nd}_{9.7}\text{Fe}_{84}\text{Mo}_{6.3}$ shows good exchange spring magnetic behavior and its minor loop is also shown.

Table 2 Summary of the observed magnetic properties of all the alloys studied.

Starting composition	Phase formed by annealing	Optimum annealing temp. (K)	Optimum nitrogenation temp. (K)	M _s (T)	Br (T)	H _c (kA/m)	(BH) _{max} (kJ/m ³)	Spring Back (%)
Nd ₉ Fe ₈₀ V ₁₁	α -Fe Nd(Fe,V) ₁₂	1123	723	0.98	0.59	104	20	
Nd ₉ Fe ₈₅ Mo ₆	α -Fe Nd(Fe,Mo) ₁₂	1073	723	1.25	0.92	56	20	
Nd ₉ Fe ₈₂ Mo ₉	α -Fe Nd(Fe,Mo) ₁₂	1073	723	1.12	0.83	64	21	
Nd ₉ Fe ₈₀ Mo ₁₁	α -Fe Nd(Fe,Mo) ₁₂	1073	773	0.70	0.50	320	28	
Nd _{9.7} Fe ₈₄ Mo _{6.3}	α -Fe Nd(Fe,Mo) ₁₂	1073	673	1.12	0.80	207	48	50

Fig.5 X-ray diffraction patterns showing the relative variation in the intensities of the α -Fe and the Nd(Fe,Mo)₁₂N_x peaks with the nitrogenation temperature. All the samples were annealed at 1073 K for 7.2 ks in vacuum.

4 Conclusions

1. Mechanical alloying and a two stage heat treatment results in a mixture of hard magnetic phase Nd(Fe,TM)₁₂N_x (where TM=V,Mo) and soft magnetic phase α -Fe.
2. The optimum magnetic properties were observed in Nd_{9.7}Fe₈₄Mo_{6.3} alloy annealed at

Fig.6 Variation in the coercivity and remanence of Nd_{9.7}Fe₈₄Mo_{6.3} samples with the nitrogenation temperature.

Fig.7 Variation in the maximum energy product (BH)_{max} of Nd_{9.7}Fe₈₄Mo_{6.3} samples with the nitrogenation temperature.

1073 K for 1.8 ks and nitrided at 673 K for 7.2 ks with a maximum energy product of 48 kJ/m³ and a spring back of 50%.

3. Nitrogenation of Nd_{9.7}Fe₈₄Mo_{6.3} at various temperature shows that beyond 673 K increase in the nitrogenation temperature results in the decrease of (BH)_{max} due to the large variation in coercivity.

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