Influence of High-Pressure Nitrogenation on the Structure, Magnetism and Microwave Absorption Properties of $\text{SmFe}_{10}\text{Mo}_2$

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Abstract Nitrogenation of $\text{SmFe}_{10}\text{Mo}_2$ powders was performed in a self-made furnace under a high-purity N_2 atmosphere up to 40 MPa at 500 °C. Upon nitrogenation at atmospheric pressure, the lattice parameters a and c increase by 0.5% and 2.7%, respectively, whereas the Curie temperature T_C increases from 519 to 633 K. With further increasing the nitrogenation pressure to 20 and 40 MPa, the 1:12 main phase starts to decompose and a large amount of Mo and α -Fe precipitates. This leads to variation of Mo concentration in the 1:12 phase and causes a sharp decrease in T_C and in the coercivity. The relative complex permittivity and permeability of paraffin– $\text{SmFe}_{10}\text{Mo}_2$ composites show multi-resonant behavior. After nitrogenation, the magnetic loss of the powders decreases, which may originate from the influence of eddy currents due to the increase in the particle size.

KEY WORDS: High-pressure nitrogenation; $\text{SmFe}_{10}\text{Mo}_2$ -based compounds; Curie temperature; Microwave absorption

1 Introduction

The intrinsic magnetic properties, especially the anisotropy, of $\text{R}_{12}\text{Fe}_{17}$ and $\text{R}(\text{Fe}, \text{M})_{12}$ (named 1:12 phase) intermetallics, with $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Mo}, \text{Al}, \text{W}$ and Si , have been found to improve dramatically upon introduction of interstitial nitrogen hydrogen or carbon which increases the unit cell volume, narrows the 3d-electron band and modifies the

crystal–field interaction [1–4]. After nitrogenation, the $\text{R}(\text{Fe}, \text{Mo})_{12}$ compounds with the ThMn_{12} structure show an increased Curie temperature, a larger saturation magnetization and a stronger uniaxial magnetocrystalline anisotropy. The compounds $\text{Nd}(\text{Fe}, \text{Mo})_{12}\text{N}_x$ [5] and $\text{Pr}(\text{Fe}, \text{Mo})_{12}\text{N}_x$ [6] have been demonstrated to be suitable as new hard magnetic materials with high coercivity of up to 6.2 kOe (4.94×10^5 A/m) and maximum energy products of up to 12.0 MGOe (95.52 kJ/m^3). So far, only few studies have been focused on the Sm nitrides with the ThMn_{12} structure. The Rietveld analysis of the XRD patterns for $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$ shows that the N atoms occupy exclusively the 2b interstitial site [7]. Most of the nitrogenation has been carried out at atmospheric pressure or even lower pressure. Therefore, it is meaningful to investigate the influence of high-pressure nitrogenation on the structure and magnetism of the ThMn_{12} -type compounds. In the present study, nitrogenation of the $\text{SmFe}_{10}\text{Mo}_2$ powders was carried out in a self-made furnace under a high-purity N_2 atmosphere of up to 40 MPa and the influence of high-pressure nitrogenation on the structure and magnetism has been studied.

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Based on soft ferromagnetic metals, the composites such as (Fe, Ni)/C [8] and Ni/Al₂O₃ [9] show excellent electromagnetic wave absorption properties mainly due to a high saturation magnetization and a high Snoek limit. Recent research has shown that the microstructure and concentration of the ferromagnetic and dielectric components have large effect on the microwave-absorption properties [10, 11]. Low-frequency dielectric studies on core-shell composite fibers of the magnesium ferrite-polyvinylidene fluoride indicate that the addition of the magnesium ferrite increases the polarization which results in an increase in the dielectric constant but decreases the dielectric loss [12]. Both the dielectric resonance and magnetic resonance are closely related to the size of the metal grains in Ni/TiO₂ [13] and Fe/TiO₂ [14] nanocomposites produced by milling and annealing. So far, few studies have focused on the microwave absorption properties of the composites based on permanent magnet materials. Recently, it has been reported that a large reflection loss (RL) from 9.6 to 18 GHz exceeding −10 dB is achieved in Nd₂Fe₁₄B/C microparticles for an absorber thickness of 1.4–2.6 mm [15]. In the present study, microwave-absorption properties of SmFe₁₀Mo₂ nanoparticles and the influence of nitrogenation have been investigated.

2 Experimental

The parent compound SmFe₁₀Mo₂ was synthesized by arc melting from 99.9% pure starting materials and annealed in vacuum at 950 °C for 2 weeks. The annealed bulk sample was pulverized by mechanical alloying for 2 h using a high-energy ball-milling machine with a rotational speed of 300 r/min and nitrogenated at 500 °C in a self-made furnace in a high-purity N₂ atmosphere at pressures up to 40 MPa. The as-prepared bulk alloy was denoted as sample A, and the ball-milled powder and the samples nitrogenated at 0.1, 20 and 40 MPa were named as sample B, C, D and E, respectively.

X-ray diffraction (XRD) was performed using CuK_α radiation by a Rigaku d/Max-γA diffractometer. The magnetic properties were measured in a vibrating sample magnetometer (Lakeshore 7407) at applied magnetic fields up to 1.8 T at the temperature range from 300 to 750 K. The toroidal specimens for measurement of the electromagnetic wave absorption properties between 2 and 18 GHz by means of a Agilent 8722ES network analyzer were prepared by uniformly mixing 40 wt% SmFe₁₀Mo₂ particles or SmFe₁₀Mo₂ nitride particles with 60 wt% paraffin. The morphology and size distribution of the particles and the energy dispersive spectrum (EDS) were examined by means of a Hitachi-3400 N scanning electron microscope (SEM).

3 Results and Discussion

3.1 Influence of High-Pressure Nitrogenation on the Structure and Magnetism of SmFe₁₀Mo₂

Figure 1 shows the XRD patterns of the bulk SmFe₁₀Mo₂, the powder and the nitrides. The bulk sample has the tetragonal ThMn₁₂-type structure with a small amount of α -Fe as impurity phase. For the powder sample milled for 2 h, a large amount of Mo is found which was precipitated from the 1:12 phase. Nitrogenation at 0.1 MPa does not change the 1:12 phase structure and only causes a shift of the reflections to lower angles, indicating the lattice expansion. With further increasing the nitrogenation pressure to 20 and 40 MPa, the 1:12 main phase starts to decompose and large amounts of Mo and α -Fe were precipitated. Previously, it has been observed that upon substitution of Ti (with smaller radius) for V in NdFe_{10.5}V_{1.5}N_y, the 1:12 main phase starts to decompose and α -Fe precipitates [16]. The measured lattice parameters *a* and *c* of the 1:12 main phase are listed in Table 1. It is worthwhile noting that upon nitrogenation, the lattice parameters *a* and *c* of the as-milled powder have increased by 0.5% and 2.7%, respectively. With further increasing pressure to 20 and 40 MPa, the lattice parameters exhibit a slight increase, indicating gradual saturation of the nitrogenation.

Figure 2 shows the SEM images EDS spectra of the samples nitrogenized at 0.1 and 40 MPa. It can be clearly seen from Fig. 2a, c that there is a quite large size distribution of the particles of the two samples. For sample C, the particle size varies roughly from 8 μ m to 100 nm,

Fig. 1 XRD patterns of bulk SmFe₁₀Mo₂ (sample A), milled SmFe₁₀Mo₂ powder (sample B), the nitrogenized SmFe₁₀Mo₂ powders under 0.1 MPa (sample C), 20 MPa (sample D), 40 MPa (sample E)

Table 1 Structural data of the $\text{SmFe}_{10}\text{Mo}_2$ powder and its nitrides

Samples	a (Å)	c (Å)
B	8.54	4.784
C	8.594	4.914
D	8.600	4.929
E	8.601	4.931

whereas for sample E, the particle size is clearly smaller with a size distribution from 4 μm to 50 nm. The decrease in particle size can be mainly ascribed to the increase in deposited $\alpha\text{-Fe}$. As it can be seen from Fig. 2b, d, Sm, Fe, Mo and N are detected by EDS and the N content increases from 22.1 at% for sample C to 22.9 at% for sample E. The results show that high-pressure nitrogenation is beneficial for increasing the N content as well as for decreasing the particle size.

The temperature dependence of the magnetization of $\text{SmFe}_{10}\text{Mo}_2$ and its nitrides was measured in a field of 0.05 T during a warming process, as shown in Fig. 3a. For the bulk sample, with increasing temperature, a magnetic phase transition from the ferromagnetic to the paramagnetic state takes place at T_C , of about 543 K, which is higher than those reported earlier [7, 17]. This can be ascribed to a slight variation of Mo concentration which can greatly influence T_C [17]. The lower T_C of 519 K for the as-milled sample B may result from the smaller particle

size and precipitation of Mo. In Fig. 3a, T_C is defined as the temperature corresponding to the minimum in the temperature dependence of the first derivative of the magnetization. It can be clearly seen that after nitrogenation at 0.1 MPa, T_C has largely increased to 633 K. It is well known that the Fe–Fe interaction is a key factor that influences the magnetic properties of Fe-rich rare earth iron compounds, and T_C strongly depends on the Fe–Fe distance [18]. As mentioned above, the N atoms in $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$ occupy exclusively the 2b interstitial sites [7]. Therefore, the increase in T_C in the present nitrides might be attributed to the change in the Fe–Fe bond length caused by the interstitial N atoms. The remarkable decrease in T_C of the samples D (417 K) and E (407 K), which have been nitrogenized at high pressure, can be ascribed to precipitation of a large amount of $\alpha\text{-Fe}$. The N contents in the nominal composition $\text{La}_{0.5}\text{Pr}_{0.5}\text{Fe}_{11.4}\text{Si}_{1.6}\text{N}_x$ for sample C nitrogenized at 0.1 MPa and sample D nitrogenized at 20 MPa were roughly evaluated by the weight difference before and after nitrogenation as $x = 0.5$ and 2.1, respectively. The N content of $x = 0.5$ is roughly in consistent with those of $\text{NdFe}_{10}\text{Mo}_2$ [19] and YTiFe_{11} nitrides [20] nitrogenized at atmospheric pressure. The present result shows that nitrogenation at high pressure results in decomposition of 1:12 main phase.

The magnetic hysteresis loops of $\text{SmFe}_{10}\text{Mo}_2$ and the nitrides at room temperature, as shown in Fig. 3b, show

Fig. 2 SEM images and EDS results of sample C nitrogenized at 0.1 MPa **a, b**, sample E nitrogenized at 40 MPa **c, d**

Fig. 3 Temperature dependence of the magnetization at 0.05 T **a**, magnetic hysteresis loop at room temperature **b** of the samples

that upon milling, the saturation magnetization (M_s) decreases from 60.3 to 50.2 Am²/kg, accompanied an increase in the coercivity from 0.04 to 0.12 T. The decrease in M_s after milling may be explained by the decrease in the grain size and by the precipitation of Mo, which leads to a decrease in main phase. The increase in coercivity should originate from the smaller particle size, the large residual stress and a large density of defects, which are introduced in the ball-milling process [21–23]. As shown in the inset of Fig. 3b, upon nitrogenation, the coercivity of the sample E nitrogenized at 40 MPa, strongly decreases to 0.018 T, which can be explained by the precipitation of soft magnetic α -Fe. The magnetic features of the SmFe₁₀Mo₂ and its nitrides are listed in Table 2.

3.2 Influence of Nitrogenation on the Microwave-Absorption Properties of SmFe₁₀Mo₂

In order to investigate the influence of nitrogenation on the microwave-absorption properties of SmFe₁₀Mo and its nitrides, the frequency dependence of the real part (ϵ') and the imaginary part (ϵ'') of the relative complex permittivity of the paraffin–SmFe₁₀Mo₂ composites and paraffin–SmFe₁₀Mo₂–nitride composites have been measured and are shown in Fig. 4a. It can be seen that for both samples B and C, ϵ' shows fluctuating behavior with three peaks around 7.4, 13.2 and 17.4 GHz, which can be attributed to the interfacial polarization and the displacement current lag at the metal/insulator interface [24]. In the ϵ'' curves, four peaks at 5.5, 10.2, 14.6 and 17.6 GHz can be observed and ϵ' exhibits a maximum and a minimum just below and above the frequency. This phenomenon is characteristic for nonlinear dielectric resonance [25].

The imaginary part of the relative complex permittivity, ϵ'' , first decreases from 0.3 to 0.1 in the 1–4 GHz range and then fluctuates from 0.02 to 0.1 in the 4–18 GHz range. The lower ϵ'' values of the paraffin–SmFe₁₀Mo₂ composites show a higher resistivity than other ferromagnetic metal-based composites, such as $\epsilon'' = 48$ –148 for Nd₂Fe₁₄B microparticles with an average particle size of 3.4 μ m [15], and $\epsilon'' = 1.6$ –2.6 for Fe(Mn)/ferrite nanocapsules [24]. This can be ascribed to the fact that there exists an oxidation layer at the surface of the SmFe₁₀Mo₂ nanoparticles which prevents the SmFe₁₀Mo₂ phase to form electrical conducting networks so that the electrical resistivity of the paraffin–SmFe₁₀Mo₂ composites is increased.

Figure 4b shows the real part (μ') and the imaginary part (μ'') of the relative complex permeability (μ_r) of samples B and C, for which μ' exhibits a decrease from 1.1 and 1.0 to 0.93 and 0.84, respectively, in the 2–4 GHz range. With further increasing the frequency, μ' shows fluctuating behavior with three peaks around 4.6, 10.2 and 15.8 GHz. The higher value of μ' for the nitrogenized sample originates from the higher M_s . As shown in Table 2, after nitrogenation, M_s has been increased from 50.2 to 74.1 Am²/kg due to further precipitation of soft magnetic α -Fe. The imaginary part μ'' exhibits two broad resonance peaks at about 6.8–8.9 and 14.3–15.9 GHz. Similar broad magnetic resonance peaks have been observed in Co/TiO₂ [26] and Ni/Al₂O₃ [9] nanocomposites. The multi-resonance peaks, as shown in Fig. 3b, can be defined as “exchange mode” resonance and are ascribed to the small size effect, the surface effect and spin-wave excitations [24]. The resonance frequency depends on the radii of the particles. In comparison with the as-milled sample, the nitrogenized

Table 2 Magnetic features of $\text{SmFe}_{10}\text{Mo}_2$ and its nitrides

Samples	M_s (Am^2/kg)	H_{cj} (T)	T_C (K)
A	60.3	0.04	543
B	50.2	0.12	519
C	74.1	0.04	633
D	69.1	0.019	417
E	67.8	0.018	407

sample shows a lower μ'' value, indicating a lower magnetic loss. This may originate from the influence of eddy currents due to the increase in particle size in the nitro- genation process. The RL value was calculated according to the transmission line theory and is shown in Fig. 5; a largest RL of -5.2 dB is obtained for the as-milled nanoparticles at 15 GHz for an absorber thickness of 9 mm. The RL value is higher than the 3 dB for $\text{Nd}_2\text{Fe}_{14}\text{B}$ microparticles [15] but lower than the 13.2 dB for $\text{Nd}_2\text{Fe}_{14}\text{B/C}$ paraffin mainly due to the increased dielectric loss from the enhancement of resistivity by the dielectric component C. It is observed that the RL values do not exceed -5 dB in the 2–18 GHz range and the largest RL value is -4 dB at 14.8 GHz for the $\text{SmFe}_{10}\text{Mo}$ nitride nanoparticles. The decrease in microwave absorption effect after nitro- genation can be mainly ascribed to the lower magnetic loss. The frequency corresponding to the largest RL is consistent with the frequencies of the magnetic

Fig. 5 Frequency dependence of the reflection loss of sample A **a**, sample C **b** dispersed in paraffin

resonance and the dielectric resonance, as shown in Fig. 4, showing that the main microwave absorption originates from a combined effect of magnetic and dielectric loss.

Fig. 4 Frequency dependence of the relative permittivity **a**, **c**, the relative permeability **b**, **d** of $\text{SmFe}_{10}\text{Mo}_2$ and its nitride dispersed in paraffin

4 Conclusions

Upon nitrogenation at atmospheric pressure, the lattice parameters, a and c , of $\text{SmFe}_{10}\text{Mo}_2$ show a large increase by 0.5% and 2.7%, respectively, and the Curie temperature T_C strongly increases from 519 to 633 K. High-pressure nitrogenation at 40 MPa leads to decomposition of the 1:12 main phase, as a result of which T_C strongly decreases to 407 K, accompanying a decrease in the coercivity to 0.018 T. The largest RL of -5.2 dB is obtained for the as-milled nanoparticles at 15 GHz for an absorber thickness of 9 mm. After nitrogenation, the microwave absorption effect decreases mainly due to the decrease in magnetic loss, which may originate from the influence of eddy currents.

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