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Neutron Powder Diffraction***

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A Study of Nitrogenation of a $\text{NdFe}_{12-x}\text{Mo}_x$ Compound

by In-situ Neutron Powder Diffraction

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The effects on the crystal lattice of a $\text{NdFe}_{12-x}\text{Mo}_x$ ($x \cong 1.7$) compound which contained ~12 vol% of bcc-Fe were studied by neutron powder diffraction during controlled nitrogenation over the 25°-600°C temperature range. The sample inside the furnace was connected to a closed volume of ultra-pure nitrogen gas while neutron data were collected over regular time intervals during sequential heating. Substantial nitrogen absorption occurred between 500° to 600°C. During the nitrogenation process the $\text{NdFe}_{12-x}\text{Mo}_x\text{N}_y$ lattice expanded while the bcc-Fe lattice contracted. An increasing decomposition of the compound into bcc-Fe at 600°C was observed. The average size of the $\text{NdFe}_{12-x}\text{Mo}_x\text{N}_y$ crystalline grains decreased starting at ~300°C, reaching a minimum at ~500°C and then increased markedly at higher temperatures. The development of lattice strains, on the other hand, showed an opposite trend, i. e., a maximum at 500°C. A correlation of structural modification of the crystalline phases and the nitrogenation process is discussed.

I. Introduction

Interstitial introduction of non-metallic atoms such as N, C or B into rare-earth (R) transition-metal (TM) compounds is one of the effective methods for fabricating new hard magnetic materials with improved properties. The method of gas-phase interstitial modification (GIM) has been applied to two families of R-TM intermetallics, the 2:17 and the 1:12 systems, with $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ and $\text{NdFe}_{12-x}\text{Mo}_x\text{N}_y$ being the leading targeted materials. Depending on the dissociation energy of the gas molecules, the strain-stress conditions of the lattice, and the nature of the gas-lattice interaction, these metastable phases of nitrides are formed within a relatively narrow temperature window. A considerable amount of investigations of the reaction mechanism and phase formation have been carried out for the $\text{Sm}_2\text{Fe}_{17}\text{N}_y$ compounds using GIM method.¹⁻⁵ The corresponding behavior of the $\text{NdFe}_{12-x}\text{Mo}_x\text{N}_y$ system, on the other hand, has not been well characterized.

The crystal structure of the parent compounds of the 1:12 family, $\text{RFe}_{12-x}\text{M}_x$ ($\text{M} = \text{Mo}, \text{Ti}, \text{V}, \text{Cr}, \text{W}$ or Si) is based on the ThMn_{12} -type body-centered tetragonal structure (space group $I4/mmm$, 2 formula units per cell).⁶ The inclusion of M atoms is essential to the stabilization of the ThMn_{12} structure. In the case of $\text{RFe}_{10}\text{Mo}_2$, the R, and Fe atoms occupy the 2a and (8i, 8j, 8f) sites, respectively, and the Mo atoms preferably occupy the 8i site. Upon nitrogenation the lattice expands, causing a narrowing of the Fe 3d band and thereby a larger saturation moment and higher Curie temperature. Since the N atoms occupy the 2b site which is in close proximity to the R atoms, the crystalline electric fields surrounding the R atoms are modified significantly. In $\text{RFe}_{12-x}\text{Mo}_x\text{N}_y$ the magnetic anisotropy changes from planar (for $y = 0$) to uniaxial along the

c-direction. The magnetic properties of $RFe_{12-x}Mo_x$ and its $RFe_{12-x}Mo_xN_y$ ($y < 0 \leq 1$) have been investigated by many workers.⁷⁻¹⁶

As the formation of $RFe_{12-x}M_xN_y$ occurs within a rather limited composition range ($1.5 < x < 2.5$ and $0 < y < 1$), many authors reported the observation of impurity phases, most often α -Fe, in the parent and/or nitrogenated materials.^{7-12, 15, 16} This difficulty has prompted an attempt in synthesizing $NdFe_{10}Mo_2$ using a polymer-network gel process.¹⁷ Concerns about the stability of the 2:17 compounds have led to numerous investigations of the MIG process.^{1-5, 18} During the nitrogenation of Sm_2Fe_{17} , the diffusion of nitrogen into the bulk of particles via extended defects on the surfaces, the development of lattice strains, and the decomposition of the materials at high temperatures were studied by several workers.^{1, 3, 5} Similar studies of the $NdFe_{12-x}Mo_xN_y$ system, to the best of our knowledge, have not been reported. In this paper we present the results of an *in-situ* neutron-diffraction study of the nitrogenation process of a $NdFe_{10.3}Mo_{1.7}$ compound.

II. Experimental Details

The $NdFe_{10.3}Mo_{1.7}$ sample was prepared by arc melting under a purified argon atmosphere from the elemental materials of at least 99% purity, followed by vacuum annealing at 950°C for a week. After cooling, the sample was ground into a powder with particle size, examined by optical microscopy, about 20 to 30 μm . X-ray diffraction analysis, carried out on a Regaku D/Max-2000 diffractometer, showed the $TnMn_{12}$ -type structure of the $NdFe_{10.3}Mo_{1.7}$ compound and a small amount of bcc α -Fe.

The neutron diffraction experiment was performed using a time-of-flight powder diffractometer SEPD at the Intense Pulsed Neutron Source of Argonne National Laboratory. The powder (~20g) was held inside a cylindrical, thin-wall vanadium tube. Four layers of very fine stainless-steel screens were laid at the open bottom and vent holes were left at the top of the tube to allow permeation of N₂ gas. The sample tube was placed inside an insert of the furnace also made with vanadium which was connected to a manifold of a gas handling apparatus filled with 1 liter 99.999% pure nitrogen gas at 1 atm pressure and room temperature. After repeated purging, the nitrogen gas was expanded into the furnace insert, and the pressure was monitored throughout the experiment. The data were collected by detectors situated at mean scattering angles of $\pm 90^\circ$ for which a resolution of $\Delta d/d = 0.5\%$ can be achieved (d is the atomic plane spacing). By virtue of the highly collimated neutron entrance and exit in a 90° -scattering geometry and the negligible neutron coherent scattering amplitude of vanadium, Bragg-scattering intensity solely from the sample was recorded. The sample temperature, monitored by thermocouples above and below the sample, were controlled at a selected temperature to within 10°C in all runs. The diffraction data were collected every hour as the temperature was raised from room temperature to $\sim 600^\circ\text{C}$. At about 450° , 500° , 550° and 600°C several 1h runs were made in order to study the kinetics of N₂ absorption. A marked drop of pressure was observed at 500°C and continued over several hours, indicating a gradual absorption of nitrogen into the powder. No attempt was made to wait till the saturated absorption before raising to the next temperature. The data were analyzed by the Rietveld refinement technique using the Generalized Structural Analysis System (GSAS) computer code.^{19, 20}

III. Results and Discussion

Fig. 1 shows a portion of the diffraction pattern typical of runs at 134° and 596°C. The fresh sample prior to nitrogenation contains a major phase of $\text{NdFe}_{10.3}\text{Mo}_{1.7}$ and a minor phase (~12 vol%) of bcc α -Fe. As the temperature increases from 24° to ~450°C, the unit-cell volume of both phases increase at a normal rate as expected from thermal expansion. At ~500°C, however, the salient drop of the nitrogen gas pressure in conjunction with a shift of the d-spacing and the intensities of the Bragg reflections indicate clearly the formation of nitride $\text{NdFe}_{10.3}\text{Mo}_{1.7}\text{N}_y$. The weighted R-factors of the 2-phase structural refinements varies from ~8% at room temperature to ~12% at 600°C. Fig. 2 shows the unit-cell volume of the nitride and α -Fe phases as well as the 2b site occupancy of nitrogen and the α -Fe volume fraction as a function of temperature. It can be seen that over a 7h-period at 500°C the unit cell of $\text{NdFe}_{10.3}\text{Mo}_{1.7}\text{N}_y$ expands continuously as more N atoms diffuse into the lattice whereas the bcc unit cell of the α -Fe lattice contracts. Furthermore, since the 2b site is located at the mid-point of two R atoms along the c-axis, the unit-cell expansion of the nitride is highly anisotropic, i. e., larger in the c-direction. The same behavior occurs at 500° and 600°C. Meanwhile, as y increases, the volume fraction of α -Fe also increases from 15% at 400°C to 25% in the last run at 600°C. Therefore, as more N atoms are incorporated into the Nd-Fe-Mo compound, the lattice expands and exerts compressive stresses on the α -Fe domains in the sample. At increasing temperatures the material becomes less stable, as can be seen from the accelerated precipitation of α -Fe phase.

Information regarding the average crystalline grain size and the lattice microstrains of the nitride can be obtained from the Rietveld refinements of the diffraction data.¹⁹ As shown in Fig.

3 the size and strains of the Nd-Fe-Mo domains do not change significantly up to about 300°C. Above ~300°C the coherency of the crystalline domains decreases rapidly, as indicated by the reduction of average grain size and the rise of lattice strains. These effects are largest at about 500°C where nitrogen diffusion rate is near a maximum (see Fig. 2), and the behavior reverses precipitously, i. e., increasing grain size and reducing strains, between 500° and 600°C. The signals from the α -Fe phase are too weak to warrant similar grain-size and strain analysis. These results enable us to speculate the following scenario. Below 300°C nitrogen diffusion into the sample is minimal, perhaps lacking the thermal and gas-solid interaction energies to activate the dissociation of nitrogen molecules. At ~300°C N atoms begin to diffuse and interact with the atoms on the intergranular boundaries of the $\text{NdFe}_{10.3}\text{Mo}_{1.7}$ particles. It is not until about 400°C when N atoms interact with the Fe (and Nd) atoms in the bulk of the particles, forming chemical bonds through hybridization of the N-2p and Fe-3d states. Presumably N diffuses into the bulk through defect structures extended inward from the surface while imposing expansive pressure. Consequently, the homogeneity of the long-range atomic order is degraded and increasing microstrains are generated within crystalline domains in the temperature interval of 400° - 500°C. Above 500°C the nitrogenated domains are annealed to form larger and more relaxed crystalline grains. Concurrent with these processes the α -Fe particles are under compressive stress from the neighboring nitride domains and more α -Fe phase is nucleated in the sample.

In summary, the present *in-situ* neutron diffraction measurements enable a quantitative analysis of the nitrogenation process of a $\text{NdFe}_{10.3}\text{Mo}_{1.7}$ compound over a crucial temperature range of 300° - 600°C in terms of nitrogen diffusion, phase morphology, grain growth and strains development. Investigations of nitrogenation of $\text{Sm}_2\text{Fe}_{17}$ have been studied by Christodoulou

and Takeshita⁵ using x-ray diffraction and thermomagnetic analysis (TMA), and by Colucci and co-workers³ using TMA and electron probe microanalysis. Electronic band calculations of model compounds within the $RFe_{12-x}Mo_xN_y$ system have been reported by several research teams.^{10, 21-23} Our results agree qualitatively with the observations of these workers. Clearly, more studies, both experimental and theoretical, are needed to elucidate the atomic organization and microscopic phenomena associated with the GIM process in rare-earth transition-metal compounds.

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Figure Captions

Figure 1. The Rietveld profile fits of diffraction data for the $\text{NdFe}_{10.3}\text{Mo}_{1.7}\text{N}_y$ (+ α -Fe) sample at 134° and 596°C . The dots are the observed, background-subtracted intensities. The solid lines represent the calculated intensities. Tick marks of top and bottom rows indicate the positions of the Bragg reflections for α -Fe and $\text{NdFe}_{10.3}\text{Mo}_{1.7}\text{N}_y$ phases, respectively. Differences between the observed and calculated intensities are shown at the bottom of each panel.

Figure 2. The unit-cell volumes of the nitride and α -Fe lattices (a), the lattice parameters of the nitride phase (b), and the nitrogen occupancy of the 2b site in $\text{NdFe}_{10.3}\text{Mo}_{1.7}\text{N}_y$ and the volume fraction of α -Fe (c) as a function of temperature during nitrogenation. The solid lines connect the data points each of which represents 1h of data collection. There are 7, 2, and 9 data points at 500° , 550° and 600°C , respectively, some of which are overlapping. Typical uncertainties of the parameters are comparable to the size of the symbols.

Figure 3. The average crystalline grain size and lattice microstrain of $\text{NdFe}_{10.3}\text{Mo}_{1.7}\text{N}_y$ as a function of temperature during nitrogenation.





