Synthesis of $L1_2$-FeNi nanoparticles by nitrogen insertion and topotactic extraction method

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The nitrogen insertion and topotactic extraction (NITE) method was used to explore an unknown metastable phase of an FeNi alloy with an Fe:Ni ratio of 1:1. We found that partly ordered non-equilibrium $L1_2$-FeNi can be obtained through Fe$_2$Ni$_2$N as the intermediate nitride phase. The experimental results of both x-ray diffraction and transmission electron microscopy with energy dispersive x-ray spectrometry are consistent in identifying the denitrided material as $L1_2$-FeNi. Ni atoms preferentially occupy the corner sites in an estimated 96% of cases. No significant difference was found in the magnetization curves between the precursor of $A1$-FeNi and $L1_2$-FeNi particles. Our results suggest that the NITE method is not only a useful way for synthesizing fully ordered alloys of equilibrium phases such as $L1_0$-FeNi but also for creating metastable phases like $L1_2$-FeNi.

Key words: soft magnetic material, super lattice structure, nanoparticle

1. Introduction

An ordered alloy of $L1_0$-FeNi$^{1-3}$ with a structural transition temperature as low as 594 K$^{4,6}$ was recently synthesized using the nitrogen insertion and topotactic extraction (NITE) method.$^7$ The NITE method consists of two steps: 1) nitriding particles of a disordered alloy to synthesize an ordered nitride compound, and then 2) topotactically removing the nitrogen$^{8,9}$ while maintaining the relative atomic positions of the other elements. Using this process, high purity $L1_0$-FeNi particles are obtained if the intermediate nitride is FeNiN.$^7$ The FeNiN has a tetragonal crystal structure, in which Fe and Ni are regularly arranged in layers. FeNiN is an anti-ferromagnetic material with a Néel temperature ($T_N$) of 177 K.$^{10}$ In this structure, the FeN layers and the Ni layers are alternately stacked along the [001] direction, which is likely due to the higher affinity for Fe:N than for Ni:N.$^{11}$ Meanwhile, the only difference in the atomic positioning of FeNiN and that of $L1_0$-FeNi is that in one, the N atoms are located between Fe atoms on Fe layers or not. Therefore, $L1_0$-FeNi is produced by reducing the number of nitrogen atoms in FeNiN. Thus, the NITE method has the potential to synthesize various ordered alloys through the nitride phases. Unlike conventional metallurgical methods, the NITE technique involves the use of chemical processes in alloy synthesis. Metallic compounds synthesized by the NITE method could have many potential applications besides $L1_0$-FeNi. There are several different phases reported for an Fe-Ni-N system. Fe$_2$Ni$_2$N$^{10,12}$ is an FeNi nitride system with a lower degree of nitridation than FeNiN. For example, Fe$_2$Ni$_2$N has a perovskite structure as shown in Fig. 1 (a). In this system, the corner sites are fully occupied by Ni atoms and the face center sites are occupied by Fe and Ni atoms with a ratio of 2:1. Moreover,

![Fig. 1 Crystal structure models of (a)Fe$_2$Ni$_2$N, (b)$L1_2$-FeNi, and (c) $L1_2$-FeNi. VESTA was used for drawing the crystal structures.](image)

![Fig. 2 Fe-Ni phase diagram calculated by K.B. Reuter et al.$^{15}$](image)
the body center position is occupied by N atoms. Therefore, it would be possible to obtain an ordered alloy by performing a denitridding treatment on Fe$_2$Ni$_2$N if both the Ni and Fe atoms remain at their original positions. The expected crystal structure of the FeNi ordered alloy obtained by the denitridding treatment of Fe$_2$Ni$_2$N is shown in Fig. 1b) and can be expressed as the $L1_2$-phase of FeNi alloy. As shown in Fig. 2, such an ordered phase is not found in the phase diagram of the Fe $\cdot$ Ni system as reported by Ying · Yu Chang et al.\textsuperscript{13-17} This structure is similar to that of Fe$_3$Ni except for the composition ratio of Fe to Ni.

In this study, we demonstrate the process of synthesizing ordered alloys of FeNi other than $L1_2$ FeNi by the NITE method. A nitride of Fe$_2$Ni$_2$N particles are transformed into $L1_2$ FeNi alloys through the NITE process.

2. Experiment

The preparation process of Fe$_2$Ni$_2$N is described as follows. FeNi nanoparticles with two different mean diameters of 30 nm and 60 nm supplied by Nisshin Engineering as a starting material, were synthesized by the thermal plasma method. In the nitriding process starting from the particles with a 60 nm mean diameter, a single phase of Fe$_2$Ni$_2$N was obtained, whereas the experiments using 30 nm particles sometimes produced FeNiN as a second phase. Therefore, subsequent experiments were performed using particles with a diameter of 60 nm. The composition ratio of Fe and Ni in the raw material determined by X-ray fluorescence spectrometers (XRF) was Fe$_{64.5}$Ni$_{35.5}$. Fe$_2$Ni$_2$N was then obtained from an FeNi alloy in the form of nanoparticles in an ammonia flow.\textsuperscript{8} The nitriding treatment was performed in an electric furnace capable of heat treatment in an ammonia atmosphere. Approximately 1 g of FeNi nanoparticles are placed in a furnace on a quartz boat. The heat treatment was performed at 300 °C for 10 h while ammonia gas was flowing at 1 L/min. Next, heat treatment was performed at 300 °C for 1 h while hydrogen gas was flowing at 1 L/min, which is the denitridding process. The purity of both ammonia and hydrogen gases used for the nitriding and denitridding processes, respectively, was greater than or equal to 99.999%. These preparation processes were optimized for the single phase formation of $L1_2$ FeNi nanoparticles.

For crystal structure analysis, an X-ray diffractometer (XRD) by Rigaku was used. Fe$K_0 \gamma = 1.75653$ Å was used as an X-ray source in order to simplify the distinction between Fe and Ni. The atomic mapping of the crystal structure was performed with a transmission electron microscope with energy dispersive x-ray spectrometry (TEM-EDX). In order to investigate the magnetic properties, the magnetic field magnetization measurement was performed at room temperature with a vibrating sample type magnetometer (VSM).

3. Results

The XRD measurement results for the particles before and after the NITE treatment are shown in Fig. 3. Experimentally obtained XRD patterns are shown in the top portion and reference patterns are shown below. The crystal structure used to calculate the XRD pattern for Fe$_2$Ni$_2$N was reported by Arnot et al.\textsuperscript{8} For Fe$_3$FeNi, we referred to the Inorganic Crystal Structure Database Collection Code (ICSD) #103556. Since the crystal structure of $L1_2$ FeNi has not been reported, we obtained both the Bragg positions and the intensities by assuming an ordered fcc structure with the lattice parameter of $a = 0.358$ nm, which is the same as that of the Fe$_3$ alloy. The inset on the left side of Fig. 3 is an enlargement of the plot corresponding to the angles between $2\theta \approx 24$ and 44°. As shown in Figs. 3 (a) and (b), the position and intensity of the diffraction lines of the FeNi alloy are changed by the nitriding treatment. The diffraction peak observed at around 38° can be assigned to NiFe$_2$O$_{311}$. The oxide phase could be caused by the surface oxidation reactions that occur when taking the alloy out of the furnace. Since the obtained diffraction lines coincide very well with the Fe$_2$Ni$_2$N shown in the reference,\textsuperscript{8} we can conclude that a single phase of Fe$_2$Ni$_2$N was synthesized by the nitriding process. The observed lattice parameters for the (Fe,Ni)-N alloy suggests that the composition ratio of (Fe,Ni):N = 4:1 when taking Vegard’s law into account. In order to estimate the site occupation elements in Fe$_2$Ni$_2$N, we compared the diffraction intensities $I(h k l)$ for the $(h k l) = (0 0 1)$ and $(h k l) = (1 1 1)$ peaks. The following formula was used for the calculation.

\[ I(h k l) \propto L_p(\theta) \cdot |F_{hkl}|^2 \quad (1) \]

\[ F_{hkl} = \sum_{n=1}^{N} f_n \exp(2\pi i(hx_1 + ky_1 + lz_1)) \quad (2) \]

![Fig. 3 XRD patterns of (a) raw material, (b) nitrided, (c) denitrided sample.](image-url)
\[ f = f_0 + f' + if''. \]  

The parameters shown here are \( \theta \) : Bragg angle, \( L_p \) : Lorentz polarization factor, \( F \) : crystal structure factor, \( f_0 \) : atomic scattering factor of the \( n \)th atom in the unit cell, \( (x_n, y_n, z_n) \) : the coordinates of the \( n \)th atom, \( (h, k, l) \) : XRD indices, \( f_0 \) : Atomic scattering factor neglecting the binding force of electrons in the atom, \( f', f'' \) : anomalous scattering factor.

The calculated result for the ordered Fe\(_2\)Ni\(_2\)N is \( I(001)/I(111) = 0.0367 \). While the experimentally obtained ratio is \( I(001)/I(111) = 0.036 \). These results are very close to those of the ideal Fe\(_2\)Ni\(_2\)N structure in which the corner sites are preferentially occupied by Ni atoms.

Subsequently, the XRD result of the denitriding sample is shown in Fig. 3 (c). The Bragg peaks appear at the same positions as those of A1-FeNi, which is the starting material, indicating that the denitriding treatment completely removes nitrogen atoms from Fe\(_2\)Ni\(_2\)N and reproduces an FeNi alloy. Although surface oxidation treatment was performed after the denitriding process, no oxide peak was observed. This is thought to be because the oxide was reduced by the heat treatment in hydrogen, and the volume ratio of the oxide film was reduced because the surface area of the film was reduced due to the particle sintering. Hereafter we refer to the denitriding treatment as DN. We note that in the diffraction lines of DN \( \cdot \) FeNi, additional peaks can be seen around \( 2\theta = 28.3^\circ \) and \( 2\theta = 40.4^\circ \), which are not seen in those locations for the disordered FeNi. In the case of the DN process used to produce \( L_3 \)-FeNi, both Fe and Ni atoms remain during the DN process. If a similar process occurs on our Fe\(_2\)Ni\(_2\)N particles during DN, we can expect that the DN \( \cdot \) FeNi is not a simple disordered fcc (A1) structure, but an ordered fcc structure with the sites preferentially occupied by Fe or Ni.

In order to evaluate the site distributions of Ni/Fe at the corner/face-centered positions of DN-FeNi, the relationship between the Ni occupation ratio at the corner site and the intensity of XRD was calculated. Here, RIETAN \( \cdot \) 2000 was used for the calculation of the intensity ratio. Furthermore, the Sasaki table lists the anomalous scattering factor associated with the atomic scattering factors for each nuclide and wavelength. The values obtained from the Sasaki table\(^{18} \) were \( f' = -4.6259 \) and \( f'' = 0.4742 \) for \( \lambda = 1.75653 \, \text{Å} \). The results of the calculation are shown in Fig. 4. The vertical axis shows a diffraction intensity ratio between (001) and (111), and the horizontal axis corresponds to the Ni occupation ratio at the corner position. From the results in Fig. 3 (c), \( I(001)/I(111) \) was found to be 0.47. This value indicates that the Ni occupation at the corner position was estimated to be 96%. This result shows that the position of the metal in the crystal structure is not notably changed before and after the denitriding treatment. From the XRD analysis results, we can conclude that DN \( \cdot \) FeNi is \( L_3 \)-FeNi.

The atomic mapping using TEM-EDS for DN \( \cdot \) FeNi is shown in Fig. 5. This image was observed from the (001) direction. Both Fe and Ni show a preferential distribution. The distribution of Fe seems to be

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**Fig. 4** Simulation of the relationship between Ni occupancy at the corner site and the intensity ratio of (001) and (111).

**Fig. 5** TEM observation of DN-FeNi. The images show (a) HAADF image and element mapping images of (b) Fe, (c) Ni, and (d) Fe and Ni overlay.

**Fig. 6** Hysteresis curves of the raw material of FeNi alloy and DN-FeNi alloy.
checkerboard-like, while that of Ni seems to be a square lattice. The observed distributions are consistent with the crystal structure of the $L1_2$ type\(^{19}\), where the corner site is occupied by only Ni and the face’s center site is occupied by either Fe or Ni.

In order to evaluate the magnetic properties of the obtained DN · FeNi, magnetic measurements using a VSM were carried out at room temperature. The results are shown in Fig. 6. Almost no change in coercivity was observed between the raw material and DN·FeNi. Unlike tetragonal $L1_2$-FeNi, both $A1$ · FeNi and DN · FeNi have a cubic crystal structure, so large magnetic anisotropy cannot be expected. For this reason, we believe that there was no significant change in coercivity with or without ordering. Note that the magnetization of DN·FeNi is slightly higher than that of the raw material. The magnetizations of DN·FeNi and the raw material at 5 kOe were 140 emu/g and 129 emu/g. It is considered that the composition ratio of Fe and Ni does not change during the NITE process. Therefore, this difference in magnetization is considered to be a difference in the surface oxidation state. In addition, there was no change in the magnetization process at room temperature; however there may be differences at Curie temperatures, because one is an ordered alloy and the other is a random alloy.

4. Summary

From the XRD and TEM-EDS measurements, we confirmed that the $L1_2$-FeNi alloy was synthesized as shown in Fig. 1 (b). The FeNi composition ratio is 1:1, and the analysis of the XRD diffraction intensity ratio shows that the corner site is occupied by only Ni atoms. Therefore, the face center position is randomly occupied by Fe or Ni with a 2:1 distribution. This arrangement of the Fe and Ni is the same as that in the distribution of atoms in the Fe$_2$Ni$_2$N, indicating that the topotactic denitriding treatment works in the same fashion for Fe$_2$Ni$_2$N as it does for FeNi. Comparing the magnetization curves of $A1$ · FeNi and $L1_2$-FeNi, there were no significant differences in either the saturation magnetizations or coercive forces. We note that the $L1_2$-FeNi phase reported here has not been reported elsewhere so far. The NITE method can be expected to be used widely as a new synthesis method for ordered alloys.

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