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<td>Author(s)</td>
<td>Yamamoto, Shinpei; Gallage, Ruwan; Isoda, Seiji; Ogata, Yasunobu; Kusano, Yoshihiro; Kobayashi, Naoya; Ogawa, Tomoyuki; Hayashi, Naoaki; Takahashi, Migaku; Takano, Mikio</td>
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Stability of $\alpha''$-Fe$_{16}$N$_2$ in hydrogenous atmospheres

Shinpei Yamamoto$^{a,b}$, Ruwan Gallage$^{a,b}$, Seiji Isoda$^a$, Yasunobu Ogata$^c$, Yoshihiro Kusano$^d$, Naoya Kobayashi$^i$, Tomoyuki Ogawa$^i$, Naoaki Hayashi$^i$, Migaku Takahashi$^i$, and Mikio Takano$^a$

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We revealed inherent instability of $\alpha''$-Fe$_{16}$N$_2$ in hydrogenous atmospheres due to denitrification toward $\alpha$-Fe by forming NH$_3$ at the particle surface. Coating the particle surface with SiO$_2$ to suppress formation of NH$_3$ has proven to be a simple yet powerful method to enhance stability in hydrogenous atmospheres.

Utilization of hydrogen energy, which can be produced from various renewable energy sources and emits no greenhouse gases in use, has potential to contribute to the formation of sustainable society. Replacement of fossil fuels by hydrogen gas thus has been studied for all levels of social systems covering from infrastructures to consumer devices. As we prepare to start the hydrogen society, development of materials stable in hydrogenous atmospheres is highly needed. Here we examine the stability of a new powerful magnetic material, $\alpha''$-Fe$_{16}$N$_2$, which may potentially be applied to, e.g., motors to be used for supply and transportation of hydrogen gas. As $\alpha''$-Fe$_{16}$N$_2$ has to be prepared and processed under reducing conditions, it is also important to understand behaviors in hydrogen gas.

$\alpha''$-Fe$_{16}$N$_2$ is a meta-stable compound with body-centered tetragonal (bct) structure, which is essentially $\alpha$-Fe containing the nitrogen atoms ordered on interstitial sites. This material has attracted much interest since the first report of a ‘giant’ magnetic moment. Although the formation of this phase was already reported in 1951, it was difficult to obtain monophasic samples, and this made the reported saturation magnetization ($M_s$) widely scattered. We recently have succeeded in preparing high-purity powdered samples in a large size of 10 g/batch and reported that the $M_s$ and the uniaxial magnetocrystalline anisotropy, $K_{an}$ were as high as 234 emu/g and $1 \times 10^7$ erg/cm$^3$ at 5 K, respectively. Potential use of this material for magnetic recording and microwave absorption has attracted much attention. Recently, another possible application as a permanent magnet has emerged. The maximum energy product ($BH_{max}$), the figure of merit that measures the performance of a permanent magnet, calculated using the experimentally determined $M_s$ and $K_{an}$ values reaches more than 100 MGOe, which is about 1.6 times larger than that of the currently strongest Nd-Fe-B magnet (~64 MGOe).

The $\alpha''$-Fe$_{16}$N$_2$ samples used in this study were prepared in two steps, oxide-to-metal reduction in a H$_2$ stream and subsequent metal-to-nitride conversion using an NH$_3$ stream, within a reactor chamber attached to the X-ray diffractometer used (see Electric Supplementary Information (ESI)). In the starting samples, only $\alpha''$-Fe$_{16}$N$_2$ and $\sim$7 wt% of $\alpha$-Fe were detected by XRD (see Run#0 in Figures and Tables S1 ~ S7 in ESI). The average crystallite size of the nitride estimated by using the Scherrer formula was ca. 28 ~ 36 nm (see Table S8 in ESI). For the in-situ XRD measurements, each sample was kept at a constant temperature of $T = 393, 398, 403, 413$ or $423$ K for a certain period of time ($t$) in a hydrogenous atmosphere (see ESI for details). Figures S1 ~ S5 in ESI show those collected in pure hydrogen atmosphere (Experiments A ~ E). With increasing heating time, $\alpha''$-Fe$_{16}$N$_2$ decreased while $\alpha$-Fe increased. No other crystalline phases were detected, revealing that the decomposition process gained, we have succeeded in developing a simple yet powerful method for enhancing the stability. The current results will open ways to wide applications of $\alpha''$-Fe$_{16}$N$_2$ in hydrogenous atmospheres.

Decomposition in reactive atmospheres like hydrogen gas could be very different because of possible dominance of solid-gas reactions. Here, we report a quantitative study on stability of $\alpha''$-Fe$_{16}$N$_2$ in hydrogenous atmospheres using in-situ powder X-ray diffraction (XRD). Based on the understanding about the decomposition process gained, we have succeeded in developing a simple yet powerful method for enhancing the stability. The current results will open ways to wide applications of $\alpha''$-Fe$_{16}$N$_2$ in hydrogenous atmospheres.

$\frac{\text{Fig. 1}}{}$ Schematic representation of decomposition of $\alpha''$-Fe$_{16}$N$_2$ in hydrogenous atmospheres. Formation of NH$_3$ ($k_{\text{Reac}}$) and diffusion of the interstitial nitrogen atoms ($k_{\text{Diff}}$) determine the overall reaction rate in the early and the latter stage of the decomposition, respectively.

The decomposition proceeds by intra-solid atomic rearrangements to form a 4 : 1 molar mixture of $\alpha$-Fe and $\gamma$-FeN, without releasing nitrogen. Decomposition in reactive atmospheres like hydrogen gas could be very different because of possible dominance of solid-gas reactions. Here, we report a quantitative study on stability of $\alpha''$-Fe$_{16}$N$_2$ in hydrogenous atmospheres using in-situ powder X-ray diffraction (XRD). Based on the understanding about the decomposition process gained, we have succeeded in developing a simple yet powerful method for enhancing the stability. The current results will open ways to wide applications of $\alpha''$-Fe$_{16}$N$_2$ in hydrogenous atmospheres.
where illustrated in Fig. 1, as the surface

latter stage:

t period of time (pure hydrogen atmosphere.

dependence of decomposition at various temperatures collected in

form the 4 : 1 molar mixture of solid-gas reaction pathway represented as:

$\alpha''-\text{Fe}_{16}\text{N}_2 + 3\text{H}_2 \rightarrow 16(\alpha-\text{Fe}) + 2\text{NH}_3$. (1)

This is totally different from the situations in inert atmospheres (N$_2$, Ar) where no solid-gas reactions take place and the decomposition proceeds via intra-solid atomic rearrangements to form the 4 : 1 mixture of $\alpha'-\text{Fe}$ and $\gamma'$-Fe$_4\text{N}$. (10)

In order to estimate the decomposition kinetics quantitatively, the relative weight fractions of $\alpha''-\text{Fe}_{16}\text{N}_2$ ($w_{\text{Fe}_{16}\text{N}_2}$) and $\alpha-\text{Fe}$ ($w_{\alpha}$) were estimated by the Rietveld analysis of the XRD patterns (see Tables S1 ~ S5 in ESI). The fraction of decomposition, D, can be expressed as:

$$D = 1 - w_{\text{Fe}_{16}\text{N}_2}(T, t) / w_{\text{Fe}_{16}\text{N}_2}(T, 0),$$

where $w_{\text{Fe}_{16}\text{N}_2}(T, 0)$ and $w_{\text{Fe}_{16}\text{N}_2}(T, t)$ represent the fractions of $\alpha''-\text{Fe}_{16}\text{N}_2$ before and after the H$_2$ treatment at T [K] for a certain period of time (t), respectively. Figure S9 in ESI show the time dependence of decomposition at various temperatures collected in pure hydrogen atmosphere.

It seems that the process is divided into two main parts with a boundary region centered at around $D = 0.6 \sim 0.9$. Irrespective of the heating temperature the early stage is well represented by the zero order reaction model. Figure S9a ~ e in ESI and the least-squares fitting values of $k_{\text{Reac}}$ and $k_{\text{Diff}}$ in Table 1.

As mentioned above, $\alpha''-\text{Fe}_{16}\text{N}_2$ decomposes by losing the interstitial nitrogen atoms in the form of NH$_3$. The applicability of the zero order reaction model to the early stage strongly suggests the rate determining process being the formation of NH$_3$ on the particle surface; the supply of nitrogen atoms from the inside to the particle surface is fast enough. On the other hand, for the latter stage the rate determining process is switched to the diffusion of nitrogen atoms to the surface. As schematically illustrated in Fig. 1, as the surface $\alpha-\text{Fe}$ slab becomes thicker the supply of nitrogen to the surface becomes short. It should be noted here that lattice parameters of the nitride phase change with prolonged H$_2$-treatment; $a$ increases while $c$ decreases. This tendency is prominent at higher temperatures and probably due to less N atom content than in the ideal composition.

The apparent rate constants of these processes, $k_{\text{Reac}}$ and $k_{\text{Diff}}$, can be expressed as below using an Arrhenius-type equation (M = Reac, Diff):

$$k_M = k_{0,M} \cdot \exp \left( -\Delta E_M / RT \right),$$

Table 1: Apparent rate constants.

<table>
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<tr>
<th>Experiment</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
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<tbody>
<tr>
<td>T (K)</td>
<td>393</td>
<td>398</td>
<td>403</td>
<td>413</td>
<td>423</td>
<td>413</td>
</tr>
<tr>
<td>$k_{\text{Reac}}$ (h$^{-1}$)</td>
<td>0.10</td>
<td>0.14</td>
<td>0.23</td>
<td>0.45</td>
<td>0.69</td>
<td>0.28</td>
</tr>
<tr>
<td>$k_{\text{Diff}}$ (10$^2$ h$^{-1}$)</td>
<td>0.25</td>
<td>0.42</td>
<td>0.66</td>
<td>0.76</td>
<td>2.25</td>
<td>0.91</td>
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a) Experiments A–E and F were carried out in H$_2$ and H$_2$/He mixture, respectively. See also ESI for details.

trace amount of N$_2$ was also detected (Figure S8 in ESI). Thus, it can be said that the decomposition essentially proceeds via a solid-gas reaction:

$$\alpha''-\text{Fe}_{16}\text{N}_2 + 3\text{H}_2 \rightarrow 16(\alpha-\text{Fe}) + 2\text{NH}_3.$$

The applicability of the zero order reaction model to the early stage strongly suggests the rate determining process being the formation of NH$_3$ on the particle surface; the supply of nitrogen atoms from the inside to the particle surface is fast enough. On the other hand, for the latter stage the rate determining process is switched to the diffusion of nitrogen atoms to the surface. As schematically illustrated in Fig. 1, as the surface $\alpha-\text{Fe}$ slab becomes thicker the supply of nitrogen to the surface becomes short. It should be noted here that lattice parameters of the nitride phase change with prolonged H$_2$-treatment; $a$ increases while $c$ decreases. This tendency is prominent at higher temperatures and probably due to less N atom content than in the ideal composition.

The apparent rate constants of these processes, $k_{\text{Reac}}$ and $k_{\text{Diff}}$, can be expressed as below using an Arrhenius-type equation (M = Reac, Diff):

$$k_M = k_{0,M} \cdot \exp \left( -\Delta E_M / RT \right),$$

Fig. 2 Plots of (a) ln($k_{\text{Reac}}$) and (b) ln($k_{\text{Diff}}$) vs. inverse temperature (1/T). The solid and open symbols represent the experimental data collected in H$_2$ and H$_2$/He mixture, respectively. The solid lines represent the least-squares fittings.

Fig. 3 D of the SiO$_2$-coated (red symbols) and the uncoated (black symbols) $\alpha''-\text{Fe}_{16}\text{N}_2$ plotted against t at 423 K. Inset shows typical TEM images of the SiO$_2$-coated $\alpha''-\text{Fe}_{16}\text{N}_2$. The surface is uniformly coated with SiO$_2$ layer (thickness, ca. 10 nm). For details of the SiO$_2$-coating, see ESI.

where $k_{0,M}$, $\Delta E_M$, R, and T are the frequency factor, apparent activation energy, gas constant and absolute temperature, respectively. The results of the Arrhenius plot are shown in Fig. 2. The values of $k_{0,\text{Reac}}$ and $\Delta E_{\text{Reac}}$ thus determined are 1.77 $\times$ 10$^{11}$ h$^{-1}$ and 92 kJ/mol, respectively. Formation of NH$_3$ from atomic nitrogen and gaseous H$_2$ on the surface must be multi-staged, including adsorption of H$_2$ molecule on the surface, scission of H-H bond, formation of N-H bonds, and desorption of NH$_3$ molecules from the surface. Determination of the stage most responsible for these kinetic parameters is beyond the scope of this paper. Similarly, $k_{0,\text{Diff}}$ and $\Delta E_{\text{Diff}}$ have been determined to be 3.24 $\times$ 10$^9$ h$^{-1}$ and 91 kJ/mol, respectively. Apparent activation energy for diffusion of nitrogen atoms in $\alpha$-Fe and Fe-N martensites have been reported to be ca. 71 kJ/mol for $\alpha$-Fe, 87 and 95 kJ/mol for 1.1 and 2.46 ~ 2.71 wt% nitrogen-doped Fe-N martensites, respectively.$^{13,14}$ Actual concentration of nitrogen in the denitrified layer may vary depending on, e.g., reaction time (t) and depth from the surface. However, it should be in between 0 (\text{\alpha-Fe}) and 3 wt% ($\alpha''-\text{Fe}_{16}\text{N}_2$). The obtained $\Delta E_{\text{Diff}}$ of 91 kJ/mol seems to be a reasonable value for diffusion of nitrogen atoms in such a concentration range.

To test the validity of the above analyses, we additionally studied decomposition in the equilibrium mixture of hydrogen and helium gases (Experiment F, see Figure and Table S6 in ESI). Partial pressure of hydrogen gas should have a strong effect on the rate of NH$_3$ formation on the particle surface but have little effect on the intra-particle diffusion of the interstitial nitrogen atoms. Figure S10a in ESI shows a plot of D vs. t together with...
that collected in pure hydrogenous atmosphere at the same temperature (Experiment D). Decomposition seems to slow down only in the earlier stage. The apparent rate constants, i.e., $k_{\text{Reac}}$ and $k_{\text{Diff}}$, determined by using eqs.(3) and (4) strongly support the validity of these models (see Figure S10b in ESI for the analyses); only $k_{\text{Reac}}$ decreases while $k_{\text{Diff}}$ remains almost unchanged (the open symbols in Figures 2a and b).

Apparent activation energy for decomposition is known to be a good measure of stability. The values for hydrogenous atmospheres, which are ca. 90 kJ/mol at most, are less than half that for inert atmospheres (199 kJ/mol), indicating the inherent instability of $\alpha''$-$\text{Fe}_16\text{N}_2$ in hydrogenous atmospheres. For practical application we need a method to improve the stability. Considering the crucial importance of NH$_3$-forming reaction on the surface, we carried out a proof-of-concept experiment, protection of surface from hydrogen by SiO$_2$-coating (Experiment G, see Figure and Table S7 in ESI). The time dependences of decomposition rate, $D$, at 423 K before and after the coating are compared in Fig. 3. It is definitely evident that the decomposition was markedly suppressed by the coating. Understanding of the surface coating effects in terms of coating materials and their thicknesses would be topics of forthcoming papers.

In conclusion, we have successfully revealed the decomposition processes and kinetics of $\alpha''$-$\text{Fe}_16\text{N}_2$ in hydrogenous atmospheres. The decomposition proceeds via a solid-gas reaction mechanism, i.e., loss of the interstitial nitrogen atoms by forming NH$_3$ on the surface to give $\alpha$-Fe. This is very different from the situations in inert atmospheres where decomposition proceeds by intra-solid atomic rearrangements to form 4 : 1 molar mixture of $\alpha$-Fe and $\gamma'$-$\text{Fe}_2\text{N}$. The process is divided into two main parts with a boundary region centered at around $D = 0.6$–0.9; formation of NH$_3$ on the particle surface and intra-particle diffusion of the interstitial nitrogen atoms are the rate determining processes in the early and the latter stage of the decomposition, respectively. Activation energies for these processes are ca. 90 kJ/mol at most, revealing the inherent instability of $\alpha''$-$\text{Fe}_16\text{N}_2$ in hydrogenous atmosphere. It is thus crucially important to enhance the stability for applications in hydrogenous atmospheres. Coating with SiO$_2$ is proven to be a simple yet powerful method for this purpose. The current results will open ways to wide applications of $\alpha''$-$\text{Fe}_16\text{N}_2$ in a coming hydrogen society.

This work was partly supported by the Research and Development of Alternative New Permanent Magnetic Materials to Nd-Fe-B Magnets Project from NEDO of Japan, the Japanese national project of Technology Research Association of Magnetic Materials for High-Efficiency Motors for Next-Generation Cars, and JSPS KAKENHI (No. 21226007).

Notes and references

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55 Electronic Supplementary Information (ESI) available: Details of the in-situ XRD, SiO$_2$-coating, and other characterization methods, in-situ XRD patterns (Figures S1 – S7), mass spectroscopic data (Figure S8), analyses of $D$ – $t$ data collected in H$_2$ (Figure S9) and in H$_2$/He mixture (Figure S10), Rietveld refinement results (Tables S1 – S7) and average crystallite size of the $\alpha''$-$\text{Fe}_16\text{N}_2$ sample (Table S8). See DOI: 10.1039/b000000x/
56 Calculated by using the following parameters under the assumption of 100 % orientation; $M$, at room temperature (226 emu/g), specific gravity of $\alpha''$-$\text{Fe}_16\text{N}_2$ (7.44), and $K_D$ ($= 1 \times 10^3$ erg/cm$^3$). Coercivity was assumed to be equal to the anisotropy field, $H_m$, defined as $H_m = 2K_D/M$. Volume ratio of $\alpha$-Fe to $\alpha''$-$\text{Fe}_16\text{N}_2$ is ca. 0.92 by using the following lattice constants of $\alpha''$-$\text{Fe}_16\text{N}_2$ ($a$ = 0.572 nm, $c$ = 0.630 nm) and $\alpha$-Fe ($a$ = 0.287 nm) (see Tables S1 – S7 in ESI), which leads to the expected decrease in surface area to be ca. 5 % by assuming a spherical sample shape. Thus, it is reasonable to assume that NH$_3$ forms on the surface whose area is almost constant during the decomposition. Accordingly, the linear $D$ – $t$ relationship under these reaction conditions strongly indicates that the rate determining process of this stage is formation of NH$_3$.
Coating the particle surface with SiO₂ has proven to be a simple yet powerful method to enhance stability of α”-Fe₁₆N₂ in hydrogenous atmospheres.