**Electric Supplementary Information (ESI)**

# Stability of α''-$Fe_{16}N_2$ in hydrogenous atmosphere

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***In-situ* XRD experiments:**

*In-situ* XRD measurements in hydrogenous atmospheres (Experiments A ~ G) were done using a Bruker New D8 ADVANCE diffractometer (Cu Kα radiation, λ = 1.54 Å) equipped with an Anton Paar XRK900 reactor chamber (inner volume, 400 $cm^3$). Diffraction patterns were collected in a $2\theta$ range from 41 ° to 85 ° with a step of 0.04 ° and an exposure time of 0.8 sec/step (*ca.* 970 sec/scan). Purities of $H_2$ and He gases are higher than 99.9999 %. Rietveld analyses were performed by using a commercially available program (TOPAS ver. 4.2). Details of the experiments are shown below:

**Experiments A~E**: The α"-$Fe_{16}N_2$ samples were prepared in the XRK900 reactor chamber attached to the diffractometer in two steps including reduction of iron oxide powder in $H_2$ at 573 K and nitridation in $NH_3$ at 423 K. The standard XRD patterns of the as-prepared samples (Run#0, see Figures and Tables S1~S5) were collected in the final stage of nitridation. Then, each sample was set to a certain fixed temperature of 393, 398, 403, 413, or 423 K at a rate of 12 K/min and kept at that temperature for 30 min in the He gas flow (300 $cm^3$/min). Then, the chamber was purged by $H_2$ (300 $cm^3$/min) for 10 min and the measurements were started under $H_2$ flow (50 $cm^3$/min).

**Experiment F:** This experiment was similarly performed as the Experiments A~E, except for the purging (150 $cm^3$/min $H_2$+150 $cm^3$/min He) and the measurement (25 $cm^3$/min $H_2$+25 $cm^3$/min He) gases. The *in-situ* measurement was performed at 413 K. See Figure and Table S6 for the standard XRD pattern of the as-prepared sample (Run#0).

**Experiment G**: the starting $SiO_2$-coated α"-$Fe_{16}N_2$ sample was set in the XRK900 reactor chamber in air and an XRD measurement was performed at room temperature to collect the standard pattern (Run#0, see Figure and Table S7). The *in-situ* measurement was performed at 423 K. The other procedures are similar to the Experiments A ~ E.

**Conditions for the *in-situ* XRD experiments.**

| Experiment | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| *T* [K] | 393 | 398 | 403 | 413 | 423 | 413 | 423 |
| Atmosphere | $H_2$[a)] | $H_2$ [a)] | $H_2$ [a)] | $H_2$ [a)] | $H_2$ [a)] | $H_2$ /He mixture[b)] | $H_2$ [a)] |
| Sample | *in-situ*[c)] | *in-situ*[c)] | *in-situ*[c)] | *in-situ*[c)] | *in-situ*[c)] | *in-situ*[c)] | $SiO_2$-coated[d)] |

a) $H_2$ (50 $cm^3$/min) flow.

b) $H_2$(25 $cm^3$/min) + He(25 $cm^3$/min) mixture gas flow.

c) Prepared *in-situ* by reduction of iron oxide powder in $H_2$ at 573 K followed by nitridation in $NH_3$ at 423 K.

d) Coated with $SiO_2$ *ex-situ*.

**$SiO_2$-coating of α"-$Fe_{16}N_2$ particles:** α"-$Fe_{16}N_2$ powder[1] (300 mg) was dispersed in a three neck flask containing a mixed solution of ethanol (150 ml), water (2 ml) and ammonium hydroxide (28%, 3 ml). While stirring, 5 ml of tetraethylorthosilicate (TEOS) in ethanol (6.3 % by volume) was injected into the suspension at a rate of 500 μl/h using an injection pump. Stirring continued for another 10 hrs after the addition of TEOS. Finally, particles were washed three times with ethanol, centrifuged, and dried at room temperature.

**The other characterization methods: m**ass spectroscopic analysis of gases evolved on heating up to 560 K (10 K/min) in flowing $H_2$ was performed using a TG-DTA2000SA thermogravimetric / differential thermal analysis apparatus equipped with an MS9610 quadrupole mass spectrometer (Bruker AXS). The uncoated α"-$Fe_{16}N_2$ sample for the mass spectroscopic measurement was prepared in two steps, oxide-to-metal reduction in a $H_2$ stream and subsequent metal-to-nitride conversion using an $NH_3$ stream.[1] The sample surface was slightly oxidized since the sample was handled in air before the measurement. Transmission electron microscopic (TEM) observation was performed by using JEOL JEM-1400. TEM specimens were prepared by dropping a particle-containing solution on a carbon-coated copper grid.

**Reference for the Supporting Information**

(1) Ogawa, T.; Ogata, Y.; Gallage, R.; Kobayashi, N.; Hayashi, N.; Kusano, Y.; Yamamoto, S.; Kohara, K.; Doi, M.; Takano, M.; Takahashi, M. *Appl. Phys. Express*, **2013**, *6*, 073007-1.

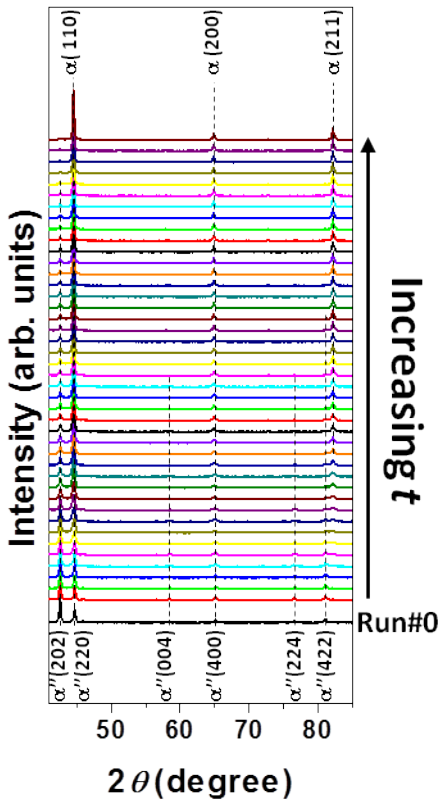


**Figure S1.** *In-situ* XRD patterns of the α"-$Fe_{16}N_2$ sample heat-treated in $H_2$ for certain periods of time (*t*) at 393 K (Experiment A). Main diffraction peaks from α"-$Fe_{16}N_2$ and α-Fe are indicated by α" and α, respectively. The bottom pattern is the one collected before the $H_2$-treatment (Run#0). For *t* of the patterns, please see Table S1.

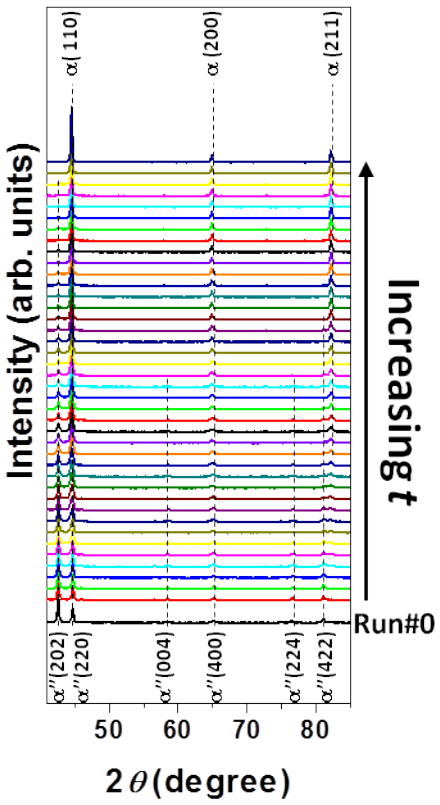


**Figure S2.** *In-situ* XRD patterns of the α"-$Fe_{16}N_2$ sample heat-treated in $H_2$ for certain periods of time (*t*) at 398 K (Experiment B). Main diffraction peaks from α"-$Fe_{16}N_2$ and α-Fe are indicated by α" and α, respectively. The bottom pattern is the one collected before the $H_2$-treatment (Run#0). For *t* of the patterns, please see Table S2.

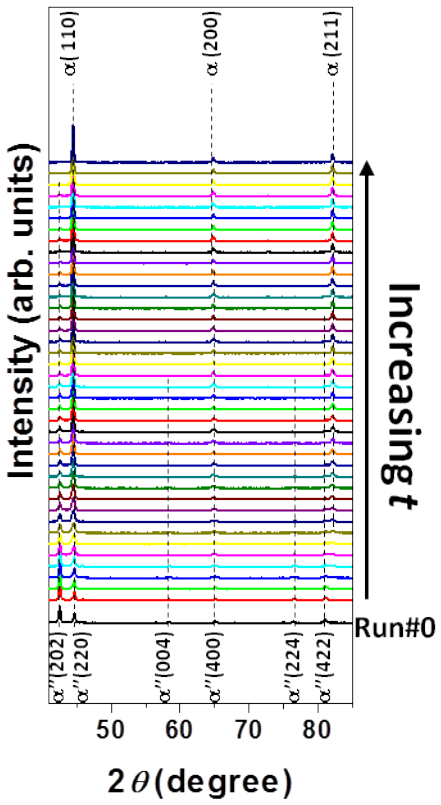


**Figure S3.** *In-situ* XRD patterns of the α"-$Fe_{16}N_2$ sample heat-treated in $H_2$ for certain periods of time (*t*) at 403 K (Experiment C). Main diffraction peaks from α"-$Fe_{16}N_2$ and α-Fe are indicated by α" and α, respectively. The bottom pattern is the one collected before the $H_2$-treatment (Run#0). For *t* of the patterns, please see Table S3.

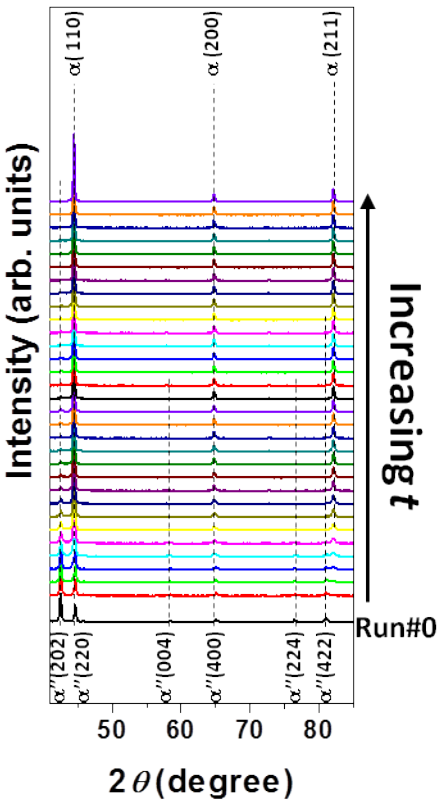


**Figure S4.** *In-situ* XRD patterns of the α"-$Fe_{16}N_2$ sample heat-treated in $H_2$ for certain periods of time (*t*) at 413 K (Experiment D). Main diffraction peaks from α"-$Fe_{16}N_2$ and α-Fe are indicated by α" and α, respectively. The bottom pattern is the one collected before the $H_2$-treatment (Run#0). For *t* of the patterns, please see Table S4.

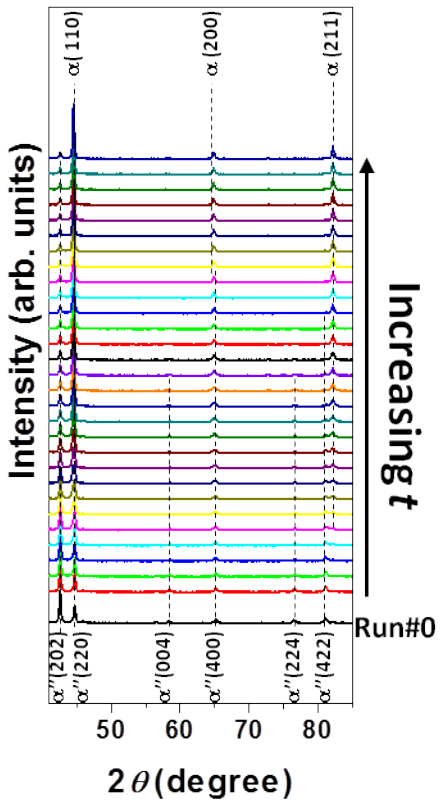


**Figure S5.** *In-situ* XRD patterns of the α”-$Fe_{16}N_2$ sample heat-treated in $H_2$ for certain periods of time (*t*) at 423 K (Experiment E). Main diffraction peaks from α”-$Fe_{16}N_2$ and α-Fe are indicated by α” and α, respectively. The bottom pattern is the one collected before the $H_2$-treatment (Run#0). For *t* of the patterns, please see Table S5.

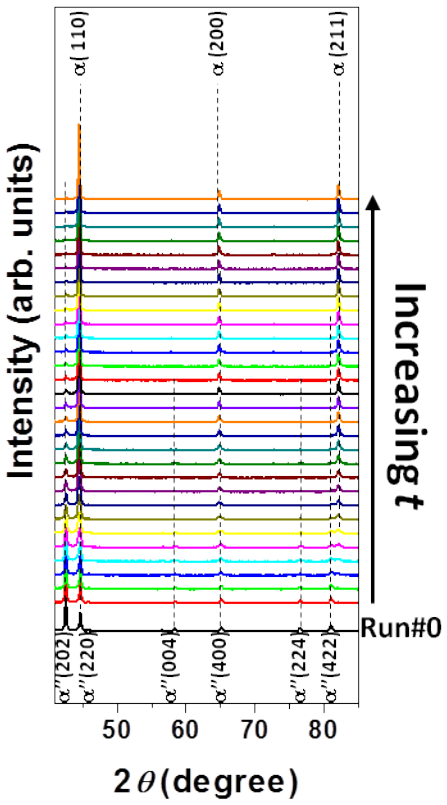


**Figure S6.** *In-situ* XRD patterns of the α”-$Fe_{16}N_2$ sample heat-treated in $H_2$/He mixture for certain periods of time (*t*) at 423 K (Experiment F). Main diffraction peaks from α”-$Fe_{16}N_2$ and α-Fe are indicated by α” and α, respectively. The bottom pattern is the one collected before the $H_2$-treatment (Run#0). For *t* of the patterns, please see Table S6.

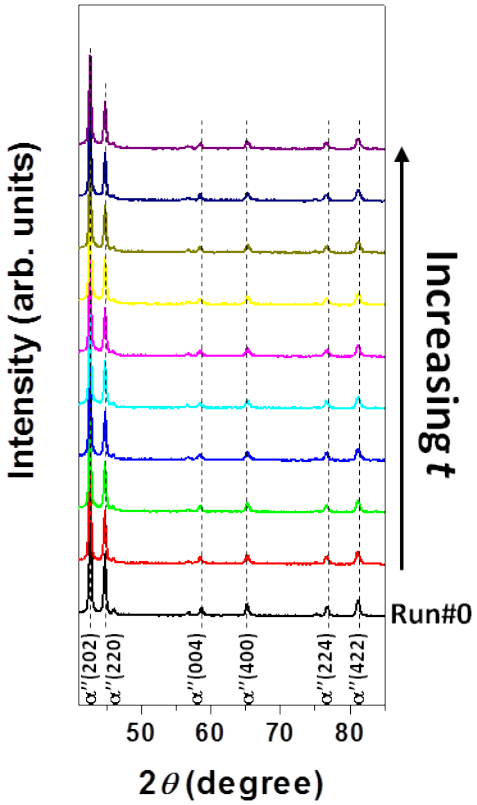


**Figure S7.** *In-situ* XRD patterns of the $SiO_2$-coated α"-$Fe_{16}N_2$ sample heat-treated in $H_2$ for certain periods of time (*t*) at 423 K (Experiment G). Main diffraction peaks from α"-$Fe_{16}N_2$ are indicated by α". The bottom pattern is the one collected before the $H_2$-treatment (Run#0). For *t* of the patterns, please see Table S7.

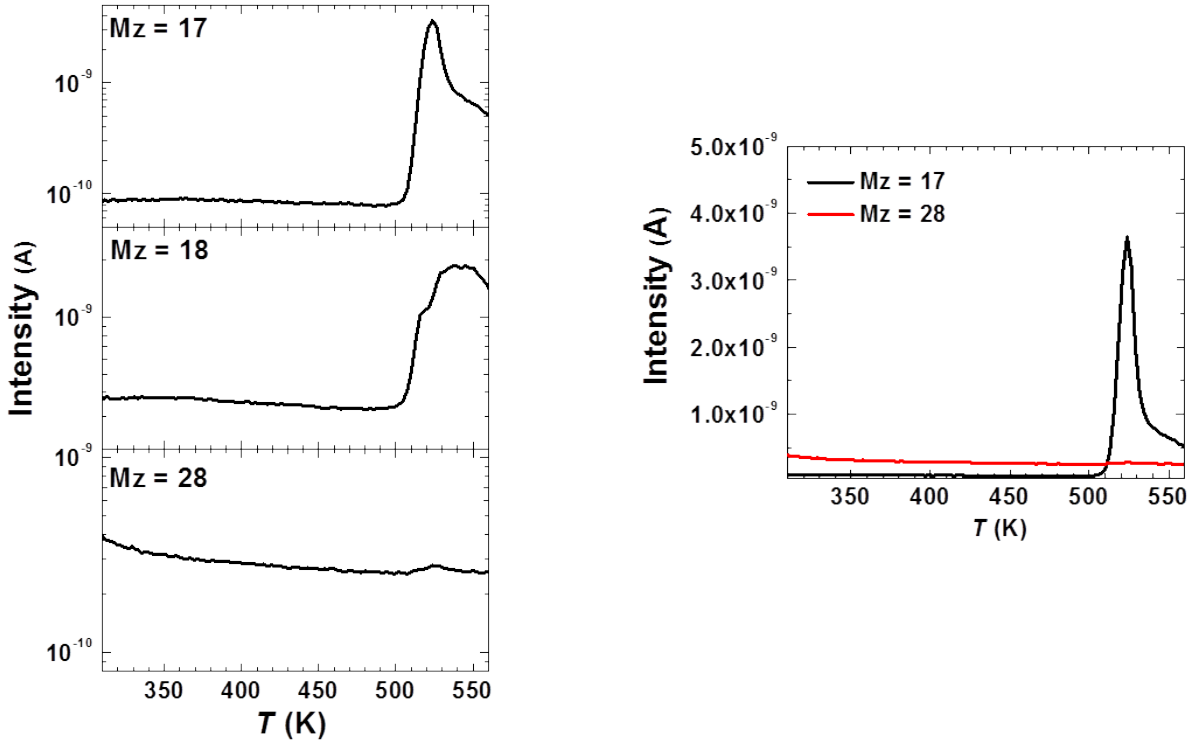


**Figure S8.** Mass spectroscopic data of the uncoated α"-$Fe_{16}N_2$ sample taken upon heating in a $H_2$ stream. The intensities for mass numbers of Mz = 17 ($NH_3$) and Mz = 18 ($H_2O$) increase from *ca.* 500 K and then decrease. Evolution of $H_2O$ is due to the reduction in the iron oxides layer on the surface of the α"-$Fe_{16}N_2$ sample (see The other characterization methods in the ESI). Evolution of $NH_3$ follows the evolution of $H_2O$ probably because $NH_3$ cannot form on the iron oxides surface. Simultaneous evolution of $N_2$ was also detected but its amount was very small (see the right panel).

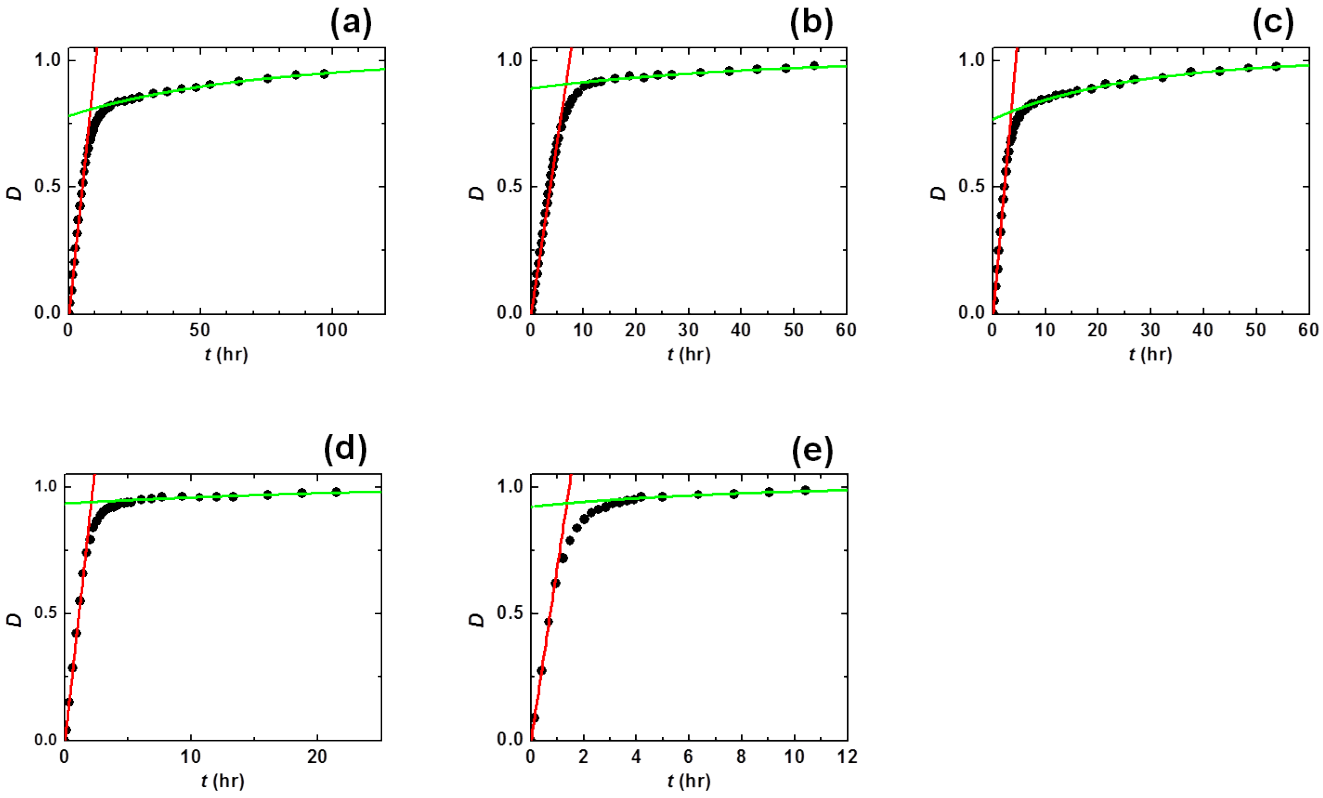


**Figure S9.** Fraction of decomposed α”-$Fe_{16}N_2$ (*D*) plotted against heating time (*t*) at (a) 393 K, (b) 398 K, (c) 403 K, (d) 413 K and (e) 423 K in $H_2$. The solid symbols represent the experimental data. The red and green lines represent the least-squares fittings using eqs.(3) and (4), respectively.

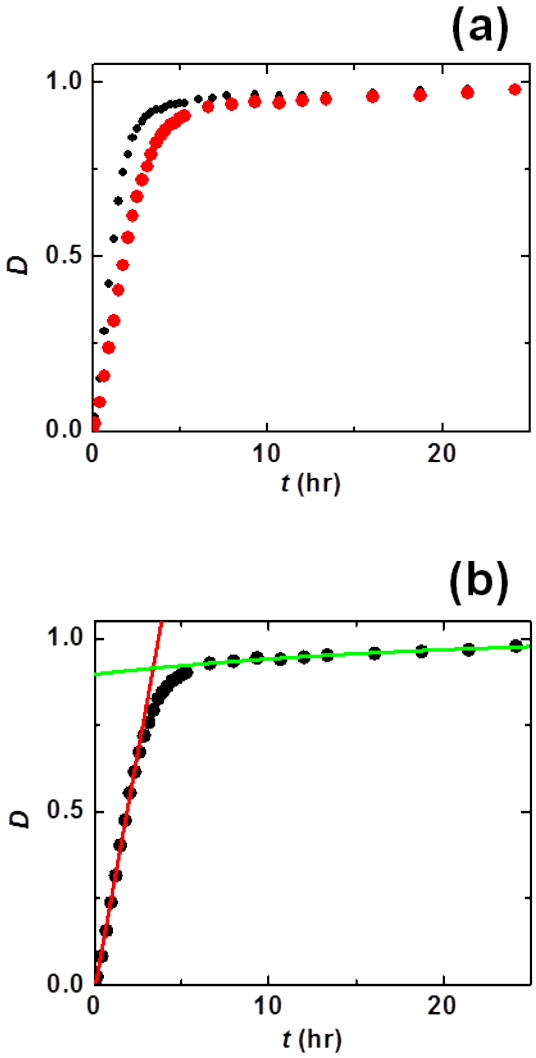


**Figure S10.** (a) Fraction of decomposed α”-$Fe_{16}N_2$ ($D$) plotted against $t$ at 413 K in $H_2$/He mixture (red symbols) and $H_2$ (black symbols). (b) Analyses of $D$ collected in $H_2$/He mixture at 413 K. The red and green lines are the least-squares fittings using eqs.(3) and (4), respectively.

**Table S1. Rietveld refinement parameters for the experiment carried out at $T = 393\ K$ under $H_2$[a] (Experiment A).**

| Run# | $t$ [hr] | $R_{exp}$[c] | $R_{wp}$[d] | S[e] | α”-$Fe_{16}N_2$ | | | α-Fe | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $a$ [Å] | $c$ [Å] | $w_{Fe16N2}$[f] | $a$ [Å] | $w_{Fe}$[g] |
| 0[b] | 0 | 2.78 | 3.45 | 1.24 | 5.71802(20) | 6.30714(36) | 0.937 | 2.87115(41) | 0.063 |
| 1 | 0.13 | 2.75 | 3.51 | 1.28 | 5.71638(20) | 6.30094(34) | 0.933 | 2.86967(38) | 0.067 |
| 2 | 0.67 | 2.76 | 3.76 | 1.36 | 5.71654(23) | 6.29927(40) | 0.893 | 2.87054(41) | 0.107 |
| 3 | 1.21 | 2.76 | 3.71 | 1.34 | 5.71650(26) | 6.29717(44) | 0.846 | 2.87094(33) | 0.154 |
| 4 | 1.75 | 2.77 | 3.80 | 1.37 | 5.71664(29) | 6.29611(49) | 0.788 | 2.87168(28) | 0.212 |
| 5 | 2.29 | 2.77 | 4.11 | 1.48 | 5.71629(35) | 6.29638(58) | 0.743 | 2.87188(26) | 0.257 |
| 6 | 2.83 | 2.77 | 4.15 | 1.50 | 5.71505(41) | 6.29518(67) | 0.692 | 2.87127(24) | 0.308 |
| 7 | 3.37 | 2.78 | 4.22 | 1.52 | 5.71663(44) | 6.29528(74) | 0.637 | 2.87162(24) | 0.363 |
| 8 | 3.91 | 2.78 | 4.35 | 1.56 | 5.71458(49) | 6.29340(79) | 0.588 | 2.87099(23) | 0.412 |
| 9 | 4.45 | 2.78 | 4.26 | 1.53 | 5.71404(50) | 6.29237(82) | 0.536 | 2.87033(21) | 0.464 |
| 10 | 4.99 | 2.79 | 4.28 | 1.53 | 5.71379(52) | 6.29410(83) | 0.491 | 2.87035(20) | 0.509 |
| 11 | 5.53 | 2.79 | 4.28 | 1.53 | 5.71402(55) | 6.29344(87) | 0.449 | 2.87002(19) | 0.551 |
| 12 | 6.07 | 2.79 | 4.21 | 1.51 | 5.71506(58) | 6.29550(90) | 0.410 | 2.87053(17) | 0.591 |
| 13 | 6.61 | 2.79 | 4.14 | 1.48 | 5.71472(58) | 6.29461(90) | 0.377 | 2.87023(16) | 0.624 |
| 14 | 7.15 | 2.79 | 4.22 | 1.51 | 5.71611(62) | 6.29382(98) | 0.345 | 2.87015(16) | 0.655 |
| 15 | 7.69 | 2.79 | 4.20 | 1.51 | 5.71581(61) | 6.29328(97) | 0.324 | 2.86991(14) | 0.676 |
| 16 | 8.23 | 2.80 | 4.16 | 1.49 | 5.71616(65) | 6.2934(10) | 0.292 | 2.86984(13) | 0.708 |
| 17 | 8.77 | 2.80 | 4.10 | 1.46 | 5.71694(64) | 6.2947(10) | 0.277 | 2.87000(12) | 0.723 |
| 18 | 9.31 | 2.80 | 3.98 | 1.42 | 5.71655(65) | 6.2934(10) | 0.258 | 2.86963(11) | 0.742 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 19 | 9.85 | 2.80 | 4.24 | 1.51 | 5.71600(72) | 6.2946(11) | 0.243 | 2.86967(11) | 0.757 |
| 20 | 10.39 | 2.80 | 4.01 | 1.43 | 5.71696(71) | 6.2948(11) | 0.229 | 2.869641(98) | 0.771 |
| 21 | 10.93 | 2.80 | 4.24 | 1.51 | 5.71736(78) | 6.2942(12) | 0.219 | 2.869575(99) | 0.781 |
| 22 | 11.47 | 2.80 | 4.04 | 1.44 | 5.71733(75) | 6.2938(12) | 0.209 | 2.869668(90) | 0.791 |
| 23 | 12.01 | 2.80 | 4.09 | 1.46 | 5.71669(77) | 6.2963(12) | 0.199 | 2.869466(87) | 0.801 |
| 24 | 12.55 | 2.80 | 4.03 | 1.44 | 5.71630(75) | 6.2953(12) | 0.196 | 2.869412(83) | 0.804 |
| 25 | 13.09 | 2.80 | 3.91 | 1.40 | 5.71670(74) | 6.2958(12) | 0.186 | 2.869469(77) | 0.814 |
| 26 | 13.63 | 2.80 | 3.96 | 1.41 | 5.71799(81) | 6.2946(13) | 0.182 | 2.869553(77) | 0.818 |
| 27 | 14.17 | 2.80 | 4.13 | 1.48 | 5.71785(88) | 6.2935(14) | 0.176 | 2.869542(78) | 0.824 |
| 28 | 14.71 | 2.80 | 4.04 | 1.44 | 5.71814(88) | 6.2938(14) | 0.171 | 2.869495(77) | 0.829 |
| 29 | 15.25 | 2.80 | 4.01 | 1.43 | 5.71673(85) | 6.2966(14) | 0.174 | 2.869480(73) | 0.827 |
| 30 | 16.06 | 2.80 | 4.00 | 1.43 | 5.71732(86) | 6.2946(14) | 0.166 | 2.869486(72) | 0.834 |
| 31 | 18.76 | 2.80 | 4.08 | 1.46 | 5.71699(91) | 6.2957(15) | 0.152 | 2.869452(70) | 0.848 |
| 32 | 21.46 | 2.80 | 4.04 | 1.44 | 5.71866(98) | 6.2906(15) | 0.148 | 2.869360(68) | 0.852 |
| 33 | 24.16 | 2.80 | 4.12 | 1.47 | 5.7179(10) | 6.2943(16) | 0.141 | 2.869423(68) | 0.859 |
| 34 | 26.86 | 2.80 | 4.10 | 1.46 | 5.7206(11) | 6.2890(17) | 0.136 | 2.869455(68) | 0.865 |
| 35 | 32.26 | 2.80 | 3.99 | 1.43 | 5.7200(12) | 6.2895(18) | 0.123 | 2.869454(65) | 0.877 |
| 36 | 37.66 | 2.81 | 4.11 | 1.46 | 5.7190(13) | 6.2925(21) | 0.115 | 2.869366(65) | 0.885 |
| 37 | 43.06 | 2.81 | 4.07 | 1.45 | 5.7203(15) | 6.2895(22) | 0.105 | 2.869405(64) | 0.895 |
| 38 | 48.46 | 2.81 | 3.91 | 1.39 | 5.7238(18) | 6.2846(26) | 0.099 | 2.869481(60) | 0.901 |
| 39 | 53.86 | 2.81 | 3.94 | 1.40 | 5.7254(19) | 6.2856(28) | 0.089 | 2.869454(60) | 0.911 |
| 40 | 64.66 | 2.81 | 3.92 | 1.40 | 5.7265(23) | 6.2812(34) | 0.077 | 2.869481(59) | 0.923 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 41 | 75.48 | 2.81 | 3.84 | 1.37 | 5.7295(27) | 6.2790(39) | 0.067 | 2.869381(56) | 0.934 |
| 42 | 86.28 | 2.81 | 3.96 | 1.41 | 5.7292(27) | 6.2829(39) | 0.054 | 2.869356(56) | 0.946 |
| 43 | 97.08 | 2.82 | 3.94 | 1.40 | 5.7285(31) | 6.2812(44) | 0.051 | 2.869381(56) | 0.949 |

a) 50 $cm^3$/min $H_2$

b) Rietveld refinement parameters of the sample determined before the $H_2$-treatment. Please see the Experimental procedures in the Supporting Information.

c) expected profile R factor

d) weighted profile R-factor

e) $S = R_{wp}/R_{exp}$

f) relative weight fraction of α"-$Fe_{16}N_2$

g) relative weight fraction of α-Fe

For details of the $R_{exp}$ and $R_{wp}$;

Young, R. A. (**1993**). "Introduction to the Rietveld method," *The Rietveld Method*, edited by R. A. Young, (Oxford University Press, Oxford), pp.1–38.

**Table S2. Rietveld refinement parameters for the experiment carried out at 398 K under $H_2$[a] (Experiment B).**

| Run# | *t* [hr] | $R_{exp}$[c] | $R_{wp}$[d] | S[e] | α”-$Fe_{16}N_2$ | | | α-Fe | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *a* [Å] | *c* [Å] | $w_{Fe16N2}$[f] | *a* [Å] | $w_{Fe}$[g] |
| 0[b] | 0 | 2.82 | 3.59 | 1.27 | 5.71829(20) | 6.30751(35) | 0.930 | 2.87141(28) | 0.070 |
| 1 | 0.13 | 2.67 | 3.78 | 1.42 | 5.71726(20) | 6.30126(34) | 0.916 | 2.86998(36) | 0.084 |
| 2 | 0.40 | 2.79 | 3.78 | 1.35 | 5.71734(23) | 6.29971(39) | 0.886 | 2.87086(36) | 0.114 |
| 3 | 0.67 | 2.79 | 4.11 | 1.47 | 5.71682(26) | 6.29764(44) | 0.855 | 2.87068(33) | 0.145 |
| 4 | 0.94 | 2.79 | 4.16 | 1.49 | 5.71704(28) | 6.29703(47) | 0.821 | 2.87091(30) | 0.179 |
| 5 | 1.21 | 2.79 | 4.36 | 1.56 | 5.71726(32) | 6.29734(53) | 0.782 | 2.87165(27) | 0.218 |
| 6 | 1.48 | 2.79 | 4.37 | 1.57 | 5.71734(35) | 6.29675(58) | 0.746 | 2.87172(25) | 0.254 |
| 7 | 1.75 | 2.79 | 4.49 | 1.61 | 5.71717(38) | 6.29709(64) | 0.703 | 2.87222(25) | 0.297 |
| 8 | 2.02 | 2.79 | 4.50 | 1.61 | 5.71712(42) | 6.29638(70) | 0.671 | 2.87192(24) | 0.329 |
| 9 | 2.29 | 2.80 | 4.64 | 1.66 | 5.71583(47) | 6.29336(75) | 0.636 | 2.87132(23) | 0.364 |
| 10 | 2.56 | 2.80 | 4.55 | 1.63 | 5.71534(48) | 6.29162(76) | 0.597 | 2.87116(22) | 0.403 |
| 11 | 2.83 | 2.80 | 4.62 | 1.65 | 5.71527(52) | 6.29167(82) | 0.561 | 2.87118(22) | 0.439 |
| 12 | 3.10 | 2.80 | 4.62 | 1.65 | 5.71494(54) | 6.29098(86) | 0.522 | 2.87089(22) | 0.477 |
| 13 | 3.37 | 2.80 | 4.64 | 1.66 | 5.71538(57) | 6.29182(89) | 0.488 | 2.87116(21) | 0.512 |
| 14 | 3.64 | 2.81 | 4.67 | 1.66 | 5.71502(60) | 6.29092(94) | 0.456 | 2.87079(21) | 0.543 |
| 15 | 3.91 | 2.81 | 4.64 | 1.65 | 5.71473(62) | 6.29028(96) | 0.422 | 2.87047(20) | 0.578 |
| 16 | 4.18 | 2.81 | 4.56 | 1.62 | 5.71504(65) | 6.2903(10) | 0.390 | 2.87047(19) | 0.610 |
| 17 | 4.45 | 2.81 | 4.57 | 1.63 | 5.71572(68) | 6.2904(10) | 0.363 | 2.87055(18) | 0.637 |
| 18 | 4.72 | 2.81 | 4.61 | 1.64 | 5.71571(72) | 6.2898(11) | 0.335 | 2.87042(17) | 0.665 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 19 | 4.99 | 2.82 | 4.47 | 1.59 | 5.71706(75) | 6.2887(11) | 0.307 | 2.87063(16) | 0.693 |
| 20 | 5.26 | 2.82 | 4.46 | 1.58 | 5.71602(77) | 6.2891(12) | 0.284 | 2.87040(15) | 0.716 |
| 21 | 5.80 | 2.82 | 4.32 | 1.53 | 5.71773(83) | 6.2876(13) | 0.244 | 2.87036(13) | 0.756 |
| 22 | 6.34 | 2.82 | 4.19 | 1.49 | 5.71925(89) | 6.2875(14) | 0.210 | 2.87044(11) | 0.790 |
| 23 | 6.88 | 2.82 | 4.32 | 1.53 | 5.7201(10) | 6.2857(16) | 0.185 | 2.870044(99) | 0.815 |
| 24 | 7.42 | 2.82 | 4.36 | 1.55 | 5.7208(12) | 6.2843(18) | 0.163 | 2.870087(93) | 0.837 |
| 25 | 7.96 | 2.82 | 4.13 | 1.46 | 5.7206(12) | 6.2880(18) | 0.140 | 2.870061(82) | 0.860 |
| 26 | 9.04 | 2.82 | 4.16 | 1.48 | 5.7208(14) | 6.2857(21) | 0.119 | 2.869896(72) | 0.881 |
| 27 | 10.12 | 2.82 | 4.08 | 1.45 | 5.7246(14) | 6.2850(21) | 0.096 | 2.870048(67) | 0.904 |
| 28 | 11.20 | 2.82 | 4.09 | 1.45 | 5.7247(16) | 6.2836(24) | 0.086 | 2.869912(63) | 0.914 |
| 29 | 12.28 | 2.82 | 4.17 | 1.48 | 5.7246(17) | 6.2840(26) | 0.080 | 2.869943(62) | 0.920 |
| 30 | 13.36 | 2.82 | 4.05 | 1.44 | 5.7254(20) | 6.2844(29) | 0.077 | 2.870023(59) | 0.923 |
| 31 | 16.06 | 2.82 | 4.14 | 1.47 | 5.7279(23) | 6.2803(34) | 0.067 | 2.869989(57) | 0.933 |
| 32 | 18.76 | 2.82 | 4.07 | 1.44 | 5.7271(23) | 6.2799(34) | 0.057 | 2.870030(57) | 0.943 |
| 33 | 21.46 | 2.82 | 4.12 | 1.46 | 5.7314(29) | 6.2737(42) | 0.062 | 2.870052(56) | 0.938 |
| 34 | 24.16 | 2.82 | 4.05 | 1.44 | 5.7491(33) | 6.2505(47) | 0.054 | 2.870021(54) | 0.946 |
| 35 | 26.86 | 2.82 | 4.00 | 1.42 | 5.7517(32) | 6.2508(47) | 0.052 | 2.870056(52) | 0.948 |
| 36 | 32.26 | 2.82 | 4.09 | 1.45 | 5.7518(38) | 6.2433(56) | 0.044 | 2.870044(53) | 0.956 |
| 37 | 37.66 | 2.82 | 3.94 | 1.40 | 5.7545(42) | 6.2442(62) | 0.039 | 2.870039(50) | 0.961 |
| 38 | 43.06 | 2.82 | 4.04 | 1.43 | 5.7555(51) | 6.2448(76) | 0.032 | 2.870060(50) | 0.968 |
| 39 | 48.46 | 2.82 | 4.35 | 1.54 | 5.7543(64) | 6.2442(94) | 0.029 | 2.870114(53) | 0.971 |
| 40 | 53.86 | 2.82 | 4.23 | 1.50 | 5.7583(47) | 6.2458(71) | 0.019 | 2.869948(51) | 0.981 |

a) 50 $cm^3$/min $H_2$

b) Rietveld refinement parameters of the sample determined before the $H_2$-treatment. Please see the Experimental procedures in the Supporting Information.

c) expected profile R factor

d) weighted profile R-factor

e) $S = R_{wp}/R_{exp}$

f) relative weight fraction of α"-$Fe_{16}N_2$

g) relative weight fraction of α-Fe

For details of the $R_{exp}$ and $R_{wp}$;

Young, R. A. (**1993**). "Introduction to the Rietveld method," *The Rietveld Method*, edited by R. A. Young, (Oxford University Press, Oxford), pp.1–38.

**Table S3. Rietveld refinement parameters for the experiment carried out at 403 K under $H_2$[a] (Experiment C).**

| Run# | *t* [hr] | $R_{exp}$[c] | $R_{wp}$[d] | S[e] | α"-$Fe_{16}N_2$ | | | α-Fe | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *a* [Å] | *c* [Å] | $w_{Fe16N2}$[f] | *a* [Å] | $w_{Fe}$[g] |
| 0[b] | 0 | 3.00 | 3.62 | 1.21 | 5.71754(26) | 6.30788(45) | 0.938 | 2.87115(47) | 0.062 |
| 1 | 0.14 | 2.97 | 3.50 | 1.18 | 5.71642(25) | 6.30248(44) | 0.937 | 2.87009(47) | 0.063 |
| 2 | 0.41 | 2.97 | 3.82 | 1.29 | 5.71656(29) | 6.29992(51) | 0.889 | 2.87085(47) | 0.111 |
| 3 | 0.68 | 2.97 | 3.97 | 1.34 | 5.71653(34) | 6.29738(58) | 0.836 | 2.87106(39) | 0.164 |
| 4 | 0.94 | 2.98 | 3.97 | 1.33 | 5.71651(39) | 6.29586(65) | 0.772 | 2.87204(31) | 0.228 |
| 5 | 1.21 | 2.98 | 3.97 | 1.33 | 5.71613(43) | 6.29592(72) | 0.703 | 2.87182(27) | 0.297 |
| 6 | 1.48 | 2.98 | 4.10 | 1.38 | 5.71516(51) | 6.29498(83) | 0.635 | 2.87186(27) | 0.365 |
| 7 | 1.75 | 2.99 | 4.52 | 1.51 | 5.71438(61) | 6.29380(99) | 0.575 | 2.87132(29) | 0.425 |
| 8 | 2.02 | 2.99 | 4.28 | 1.43 | 5.71559(58) | 6.29541(95) | 0.516 | 2.87157(25) | 0.484 |
| 9 | 2.29 | 2.99 | 4.46 | 1.49 | 5.71561(64) | 6.2956(10) | 0.468 | 2.87134(24) | 0.532 |
| 10 | 2.56 | 3.00 | 4.34 | 1.45 | 5.71611(63) | 6.2940(11) | 0.411 | 2.87106(21) | 0.589 |
| 11 | 2.83 | 3.00 | 4.32 | 1.44 | 5.71491(66) | 6.2966(11) | 0.368 | 2.87090(19) | 0.632 |
| 12 | 3.10 | 3.00 | 4.53 | 1.51 | 5.71603(74) | 6.2946(12) | 0.337 | 2.87070(19) | 0.663 |
| 13 | 3.37 | 3.00 | 4.37 | 1.46 | 5.71669(73) | 6.2928(12) | 0.303 | 2.87050(17) | 0.697 |
| 14 | 3.64 | 3.00 | 4.49 | 1.50 | 5.71616(78) | 6.2954(13) | 0.287 | 2.87036(16) | 0.713 |
| 15 | 3.92 | 3.01 | 4.57 | 1.52 | 5.71627(84) | 6.2939(13) | 0.267 | 2.87030(15) | 0.733 |
| 16 | 4.19 | 3.01 | 4.56 | 1.51 | 5.71749(93) | 6.2926(14) | 0.245 | 2.87012(15) | 0.755 |
| 17 | 4.46 | 3.01 | 4.47 | 1.49 | 5.71767(94) | 6.2929(15) | 0.235 | 2.87016(14) | 0.765 |
| 18 | 4.73 | 3.01 | 4.59 | 1.52 | 5.71653(96) | 6.2935(15) | 0.217 | 2.86997(14) | 0.783 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 19 | 5.00 | 3.01 | 4.41 | 1.47 | 5.71743(99) | 6.2945(15) | 0.212 | 2.87003(12) | 0.788 |
| 20 | 5.27 | 3.01 | 4.50 | 1.50 | 5.7170(10) | 6.2935(16) | 0.199 | 2.86988(13) | 0.802 |
| 21 | 5.81 | 3.01 | 4.47 | 1.49 | 5.7165(10) | 6.2923(16) | 0.187 | 2.86984(12) | 0.813 |
| 22 | 6.35 | 3.01 | 4.60 | 1.53 | 5.7185(11) | 6.2929(17) | 0.180 | 2.86988(12) | 0.820 |
| 23 | 6.89 | 3.01 | 4.56 | 1.51 | 5.7195(11) | 6.2911(18) | 0.171 | 2.86991(11) | 0.829 |
| 24 | 7.43 | 3.01 | 4.63 | 1.54 | 5.7179(12) | 6.2929(18) | 0.160 | 2.86981(11) | 0.840 |
| 25 | 7.97 | 3.01 | 4.57 | 1.52 | 5.7189(12) | 6.2920(19) | 0.159 | 2.86984(10) | 0.841 |
| 26 | 9.32 | 3.01 | 4.65 | 1.54 | 5.7213(13) | 6.2861(20) | 0.147 | 2.86975(11) | 0.853 |
| 27 | 10.67 | 3.01 | 4.62 | 1.53 | 5.7217(15) | 6.2863(22) | 0.141 | 2.86984(10) | 0.859 |
| 28 | 12.02 | 3.01 | 4.70 | 1.56 | 5.7196(14) | 6.2881(22) | 0.129 | 2.86971(10) | 0.871 |
| 29 | 13.37 | 3.01 | 4.58 | 1.52 | 5.7217(15) | 6.2870(23) | 0.124 | 2.86982(10) | 0.876 |
| 30 | 14.72 | 3.01 | 4.51 | 1.50 | 5.7225(17) | 6.2853(25) | 0.123 | 2.869796(93) | 0.877 |
| 31 | 16.07 | 3.01 | 4.71 | 1.56 | 5.7214(19) | 6.2850(28) | 0.112 | 2.869700(97) | 0.888 |
| 32 | 18.77 | 3.01 | 4.66 | 1.55 | 5.7242(21) | 6.2810(31) | 0.106 | 2.869657(94) | 0.894 |
| 33 | 21.47 | 3.01 | 4.81 | 1.60 | 5.7234(23) | 6.2792(34) | 0.089 | 2.869667(96) | 0.911 |
| 34 | 24.17 | 3.01 | 4.63 | 1.54 | 5.7276(29) | 6.2779(42) | 0.088 | 2.869726(89) | 0.912 |
| 35 | 26.87 | 3.02 | 4.56 | 1.51 | 5.7268(31) | 6.2778(45) | 0.072 | 2.869647(87) | 0.928 |
| 36 | 32.27 | 3.01 | 4.66 | 1.55 | 5.7327(47) | 6.2666(66) | 0.063 | 2.869598(86) | 0.937 |
| 37 | 37.67 | 3.01 | 4.73 | 1.57 | 5.7325(63) | 6.2688(90) | 0.042 | 2.869639(87) | 0.958 |
| 38 | 43.07 | 3.01 | 4.68 | 1.55 | 5.7481(68) | 6.2508(98) | 0.039 | 2.869675(78) | 0.961 |
| 39 | 48.47 | 3.02 | 4.83 | 1.60 | 5.7574(71) | 6.233(10) | 0.028 | 2.869537(78) | 0.972 |
| 40 | 53.87 | 3.02 | 4.86 | 1.61 | 5.7589(51) | 6.2437(78) | 0.024 | 2.869481(78) | 0.977 |

a) 50 $cm^3$/min $H_2$

b) Rietveld refinement parameters of the sample determined before the $H_2$-treatment. Please see the Experimental procedures in the Supporting Information.

c) expected profile R factor

d) weighted profile R-factor

e) $S = R_{wp}/R_{exp}$

f) relative weight fraction of α"-$Fe_{16}N_2$

g) relative weight fraction of α-Fe

For details of the $R_{exp}$ and $R_{wp}$;

Young, R. A. (**1993**). "Introduction to the Rietveld method," *The Rietveld Method*, edited by R. A. Young, (Oxford University Press, Oxford), pp.1–38.

**Table S4. Rietveld refinement parameters for the experiment carried out at 413 K under $H_2$[a] (Experiment D).**

| Run# | *t* [hr] | $R_{exp}$[c] | $R_{wp}$[d] | S[e] | α”-$Fe_{16}N_2$ | | | α-Fe | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *a* [Å] | *c* [Å] | $w_{Fe16N2}$[f] | *a* [Å] | $w_{Fe}$[g] |
| 0[b] | 0 | 2.38 | 3.57 | 1.50 | 5.71736(19) | 6.30683(32) | 0.941 | 2.87074(37) | 0.059 |
| 1 | 0.13 | 2.79 | 4.40 | 1.58 | 5.71687(27) | 6.30176(45) | 0.901 | 2.86985(44) | 0.099 |
| 2 | 0.40 | 2.80 | 4.89 | 1.75 | 5.71611(35) | 6.29774(60) | 0.799 | 2.87099(33) | 0.200 |
| 3 | 0.67 | 2.80 | 5.21 | 1.86 | 5.71580(49) | 6.29380(81) | 0.670 | 2.87144(28) | 0.330 |
| 4 | 0.94 | 2.81 | 5.17 | 1.84 | 5.71654(60) | 6.29424(99) | 0.543 | 2.87197(26) | 0.457 |
| 5 | 1.21 | 2.81 | 4.99 | 1.78 | 5.71546(70) | 6.2898(11) | 0.424 | 2.87106(22) | 0.576 |
| 6 | 1.48 | 2.82 | 4.81 | 1.71 | 5.71601(82) | 6.2885(12) | 0.321 | 2.87073(18) | 0.679 |
| 7 | 1.75 | 2.82 | 4.59 | 1.63 | 5.71729(94) | 6.2873(15) | 0.244 | 2.87061(14) | 0.757 |
| 8 | 2.02 | 2.82 | 4.36 | 1.55 | 5.7199(11) | 6.2831(17) | 0.194 | 2.87036(11) | 0.806 |
| 9 | 2.29 | 2.82 | 3.93 | 1.39 | 5.7210(12) | 6.2836(19) | 0.150 | 2.870342(82) | 0.850 |
| 10 | 2.56 | 2.82 | 3.83 | 1.36 | 5.7219(14) | 6.2811(22) | 0.125 | 2.870252(70) | 0.875 |
| 11 | 2.83 | 2.83 | 3.91 | 1.38 | 5.7226(16) | 6.2802(25) | 0.107 | 2.870156(64) | 0.893 |
| 12 | 3.10 | 2.82 | 3.79 | 1.34 | 5.7197(17) | 6.2858(26) | 0.092 | 2.870193(58) | 0.908 |
| 13 | 3.37 | 2.82 | 3.77 | 1.34 | 5.7254(20) | 6.2779(29) | 0.081 | 2.870235(56) | 0.919 |
| 14 | 3.64 | 2.82 | 3.65 | 1.29 | 5.7247(20) | 6.2822(30) | 0.073 | 2.870168(52) | 0.927 |
| 15 | 3.91 | 2.83 | 3.76 | 1.33 | 5.7298(24) | 6.2719(36) | 0.075 | 2.870258(53) | 0.925 |
| 16 | 4.18 | 2.82 | 3.75 | 1.33 | 5.7283(23) | 6.2738(34) | 0.067 | 2.870197(52) | 0.934 |
| 17 | 4.45 | 2.82 | 3.72 | 1.32 | 5.7247(24) | 6.2794(36) | 0.059 | 2.870156(50) | 0.941 |
| 18 | 4.72 | 2.82 | 3.80 | 1.35 | 5.7255(26) | 6.2776(39) | 0.060 | 2.870233(51) | 0.941 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 19 | 4.99 | 2.82 | 3.72 | 1.32 | 5.7291(27) | 6.2769(40) | 0.057 | 2.870229(50) | 0.943 |
| 20 | 5.26 | 2.82 | 3.80 | 1.35 | 5.7305(31) | 6.2720(45) | 0.057 | 2.870219(51) | 0.943 |
| 21 | 6.07 | 2.83 | 3.71 | 1.31 | 5.7386(42) | 6.2561(60) | 0.047 | 2.870238(48) | 0.953 |
| 22 | 6.88 | 2.83 | 3.72 | 1.31 | 5.7506(39) | 6.2478(57) | 0.043 | 2.870282(47) | 0.957 |
| 23 | 7.69 | 2.83 | 3.74 | 1.32 | 5.7490(47) | 6.2436(67) | 0.037 | 2.870261(48) | 0.963 |
| 24 | 9.31 | 2.83 | 3.73 | 1.32 | 5.7522(50) | 6.2394(72) | 0.034 | 2.870234(46) | 0.966 |
| 25 | 10.66 | 2.83 | 3.6 | 1.27 | 5.7632(80) | 6.190(12) | 0.038 | 2.870267(43) | 0.962 |
| 26 | 12.01 | 2.83 | 3.88 | 1.37 | 5.7547(85) | 6.193(13) | 0.035 | 2.870185(46) | 0.965 |
| 27 | 13.36 | 2.83 | 3.95 | 1.40 | 5.7563(98) | 6.185(15) | 0.037 | 2.870228(47) | 0.963 |
| 28 | 16.06 | 2.83 | 3.79 | 1.34 | 5.7592(98) | 6.182(15) | 0.029 | 2.870236(44) | 0.971 |
| 29 | 18.76 | 2.83 | 3.78 | 1.34 | 5.763(10) | 6.133(15) | 0.022 | 2.870209(43) | 0.978 |
| 30 | 21.46 | 2.83 | 3.75 | 1.33 | 5.751(11) | 6.130(15) | 0.019 | 2.870234(43) | 0.981 |

a) 50 $cm^3$/min $H_2$

b) Rietveld refinement parameters of the sample determined before the $H_2$-treatment. Please see the Experimental procedures in the Supporting Information.

c) expected profile R factor

d) weighted profile R-factor

e) $S = R_{wp}/R_{exp}$

f) relative weight fraction of α"-$Fe_{16}N_2$

g) relative weight fraction of α-Fe

For details of the $R_{exp}$ and $R_{wp}$;

Young, R. A. (**1993**). "Introduction to the Rietveld method," *The Rietveld Method*, edited by R. A. Young, (Oxford University Press,

Oxford), pp.1–38.

**Table S5. Rietveld refinement parameters for the experiment carried out at 423 K under $H_2$[a] (Experiment E).**

| Run# | *t* [hr] | $R_{exp}$[c] | $R_{wp}$[d] | S[e] | α”-$Fe_{16}N_2$ | | | α-Fe | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *a* [Å] | *c* [Å] | $w_{Fe16N2}$[f] | *a* [Å] | $w_{Fe}$[g] |
| 0[b] | 0 | 2.66 | 3.16 | 1.19 | 5.71766(18) | 6.30672(31) | 0.933 | 2.87070(33) | 0.067 |
| 1 | 0.14 | 2.64 | 4.83 | 1.83 | 5.71626(30) | 6.30241(52) | 0.849 | 2.87025(38) | 0.151 |
| 2 | 0.41 | 2.65 | 5.61 | 2.12 | 5.71629(50) | 6.30089(84) | 0.677 | 2.87154(29) | 0.323 |
| 3 | 0.68 | 2.66 | 5.62 | 2.11 | 5.71464(63) | 6.2960(10) | 0.496 | 2.87095(26) | 0.504 |
| 4 | 0.94 | 2.66 | 5.17 | 1.94 | 5.71553(73) | 6.2932(12) | 0.355 | 2.87051(18) | 0.645 |
| 5 | 1.22 | 2.66 | 4.69 | 1.76 | 5.71529(85) | 6.2917(14) | 0.263 | 2.87049(12) | 0.737 |
| 6 | 1.48 | 2.67 | 4.19 | 1.57 | 5.7183(10) | 6.2888(16) | 0.196 | 2.870570(88) | 0.804 |
| 7 | 1.75 | 2.67 | 4.05 | 1.52 | 5.7180(13) | 6.2888(20) | 0.150 | 2.870479(75) | 0.850 |
| 8 | 2.02 | 2.67 | 3.87 | 1.45 | 5.7187(15) | 6.2861(24) | 0.118 | 2.870419(67) | 0.882 |
| 9 | 2.29 | 2.67 | 3.97 | 1.49 | 5.7232(19) | 6.2824(28) | 0.095 | 2.870444(64) | 0.905 |
| 10 | 2.56 | 2.67 | 3.69 | 1.38 | 5.7253(21) | 6.2800(31) | 0.083 | 2.870509(57) | 0.917 |
| 11 | 2.83 | 2.67 | 3.87 | 1.45 | 5.7268(25) | 6.2764(38) | 0.073 | 2.870561(57) | 0.927 |
| 12 | 3.10 | 2.68 | 3.80 | 1.42 | 5.7282(31) | 6.2766(45) | 0.060 | 2.870447(55) | 0.940 |
| 13 | 3.37 | 2.68 | 3.77 | 1.41 | 5.7305(36) | 6.2670(52) | 0.056 | 2.870419(55) | 0.944 |
| 14 | 3.64 | 2.68 | 3.86 | 1.44 | 5.7517(39) | 6.2435(56) | 0.048 | 2.870430(55) | 0.952 |
| 15 | 3.91 | 2.68 | 3.77 | 1.41 | 5.7407(49) | 6.2565(70) | 0.046 | 2.870495(51) | 0.954 |
| 16 | 4.18 | 2.68 | 3.75 | 1.40 | 5.7398(53) | 6.2583(75) | 0.037 | 2.870483(51) | 0.963 |
| 17 | 4.99 | 2.68 | 3.78 | 1.41 | 5.7473(74) | 6.238(11) | 0.035 | 2.870426(49) | 0.965 |
| 18 | 6.34 | 2.68 | 3.74 | 1.40 | 5.749(11) | 6.189(17) | 0.027 | 2.870393(47) | 0.973 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 19 | 7.69 | 2.68 | 3.74 | 1.40 | 5.749(12) | 6.174(17) | 0.026 | 2.870351(47) | 0.974 |
| 20 | 9.04 | 2.68 | 3.97 | 1.48 | 5.757(15) | 6.108(22) | 0.018 | 2.870316(49) | 0.982 |
| 21 | 10.39 | 2.68 | 3.87 | 1.44 | 5.7603(84) | 6.122(12) | 0.013 | 2.870418(46) | 0.987 |

a) 50 $cm^3$/min $H_2$

b) Rietveld refinement parameters of the sample determined before the $H_2$-treatment. Please see the Experimental procedures in the Supporting Information.

c) expected profile R factor

d) weighted profile R-factor

e) $S = R_{wp}/R_{exp}$

f) relative weight fraction of α"-$Fe_{16}N_2$

g) relative weight fraction of α-Fe

For details of the $R_{exp}$ and $R_{wp}$;

Young, R. A. (**1993**). "Introduction to the Rietveld method," *The Rietveld Method*, edited by R. A. Young, (Oxford University Press, Oxford), pp.1–38.

**Table S6. Rietveld refinement parameters for the experiment carried out at 413 K under $H_2$/He mixture gas[a] (Experiment F).**

| Run# | *t* [hr] | $R_{exp}$[c] | $R_{wp}$[d] | S[e] | α"-$Fe_{16}N_2$ | | | α-Fe | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *a* [Å] | *c* [Å] | $w_{Fe16N2}$[f] | *a* [Å] | $w_{Fe}$[g] |
| 0[b] | 0 | 2.74 | 3.69 | 1.35 | 5.71772(19) | 6.30694(34) | 0.940 | 2.87061(37) | 0.060 |
| 1 | 0.13 | 2.70 | 4.26 | 1.58 | 5.71617(21) | 6.30222(38) | 0.918 | 2.86946(38) | 0.082 |
| 2 | 0.40 | 2.71 | 4.62 | 1.70 | 5.71636(25) | 6.29930(45) | 0.862 | 2.86989(34) | 0.138 |
| 3 | 0.67 | 2.71 | 4.67 | 1.72 | 5.71684(32) | 6.29681(55) | 0.792 | 2.87098(29) | 0.208 |
| 4 | 0.94 | 2.71 | 4.72 | 1.74 | 5.71676(37) | 6.29556(63) | 0.717 | 2.87121(25) | 0.283 |
| 5 | 1.21 | 2.72 | 4.83 | 1.78 | 5.71759(43) | 6.29574(73) | 0.643 | 2.87184(23) | 0.357 |
| 6 | 1.48 | 2.72 | 4.77 | 1.75 | 5.71743(50) | 6.29534(84) | 0.561 | 2.87174(23) | 0.439 |
| 7 | 1.75 | 2.72 | 4.67 | 1.72 | 5.71728(53) | 6.29218(89) | 0.493 | 2.87126(21) | 0.507 |
| 8 | 2.02 | 2.73 | 4.59 | 1.68 | 5.71697(55) | 6.29074(92) | 0.419 | 2.87102(18) | 0.581 |
| 9 | 2.29 | 2.73 | 4.46 | 1.63 | 5.71703(61) | 6.2911(10) | 0.362 | 2.87087(16) | 0.638 |
| 10 | 2.56 | 2.70 | 4.11 | 1.52 | 5.71738(70) | 6.2889(11) | 0.308 | 2.87051(14) | 0.692 |
| 11 | 2.83 | 2.73 | 4.36 | 1.60 | 5.71798(75) | 6.2875(12) | 0.264 | 2.87046(12) | 0.736 |
| 12 | 3.10 | 2.73 | 4.23 | 1.55 | 5.71887(85) | 6.2860(13) | 0.227 | 2.87024(11) | 0.773 |
| 13 | 3.37 | 2.53 | 4.10 | 1.62 | 5.72078(94) | 6.2838(15) | 0.194 | 2.870126(95) | 0.806 |
| 14 | 3.64 | 2.73 | 4.11 | 1.51 | 5.7204(10) | 6.2855(16) | 0.163 | 2.870084(88) | 0.837 |
| 15 | 3.91 | 2.73 | 3.95 | 1.45 | 5.7219(11) | 6.2851(17) | 0.144 | 2.870123(80) | 0.856 |
| 16 | 4.18 | 2.73 | 3.97 | 1.45 | 5.7205(11) | 6.2866(17) | 0.129 | 2.870066(76) | 0.871 |
| 17 | 4.45 | 2.73 | 3.98 | 1.46 | 5.7221(13) | 6.2849(20) | 0.114 | 2.870054(73) | 0.886 |
| 18 | 4.72 | 2.73 | 3.91 | 1.43 | 5.7231(14) | 6.2839(21) | 0.107 | 2.870057(69) | 0.893 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 19 | 4.99 | 2.73 | 3.9 | 1.43 | 5.7244(13) | 6.2816(20) | 0.098 | 2.869976(68) | 0.902 |
| 20 | 5.26 | 2.73 | 4.01 | 1.47 | 5.7270(16) | 6.2776(24) | 0.091 | 2.869909(69) | 0.909 |
| 21 | 6.61 | 2.73 | 3.90 | 1.43 | 5.7267(18) | 6.2805(27) | 0.067 | 2.869932(63) | 0.933 |
| 22 | 7.96 | 2.73 | 3.99 | 1.46 | 5.7317(22) | 6.2709(32) | 0.061 | 2.869959(62) | 0.939 |
| 23 | 9.31 | 2.73 | 4.23 | 1.55 | 5.7313(26) | 6.2723(37) | 0.053 | 2.869878(62) | 0.947 |
| 24 | 10.66 | 2.73 | 4.18 | 1.53 | 5.7337(31) | 6.2683(44) | 0.056 | 2.869948(62) | 0.944 |
| 25 | 12.01 | 2.73 | 4.11 | 1.51 | 5.7313(35) | 6.2712(50) | 0.050 | 2.869875(61) | 0.950 |
| 26 | 13.36 | 2.73 | 4.06 | 1.49 | 5.7516(33) | 6.2496(48) | 0.045 | 2.869895(56) | 0.955 |
| 27 | 16.06 | 2.73 | 4.19 | 1.53 | 5.7513(39) | 6.2459(57) | 0.041 | 2.869826(57) | 0.959 |
| 28 | 18.76 | 2.73 | 4.10 | 1.50 | 5.7461(47) | 6.2524(68) | 0.035 | 2.869861(56) | 0.965 |
| 29 | 21.46 | 2.73 | 4.17 | 1.53 | 5.7472(69) | 6.247(10) | 0.030 | 2.869818(55) | 0.970 |
| 30 | 24.16 | 2.73 | 4.18 | 1.53 | 5.7549(39) | 6.2532(60) | 0.020 | 2.869929(56) | 0.980 |

a) 25 $cm^3$/min $H_2$ + 25 $cm^3$/min He

b) Rietveld refinement parameters of the sample determined before the $H_2$-treatment. Please see the Experimental procedures in the Supporting Information.

c) expected profile R factor

d) weighted profile R-factor

e) $S = R_{wp}/R_{exp}$

f) relative weight fraction of α"-$Fe_{16}N_2$

g) relative weight fraction of α-Fe

For details of the $R_{exp}$ and $R_{wp}$;

Young, R. A. (**1993**). "Introduction to the Rietveld method," *The Rietveld Method*, edited by R. A. Young, (Oxford University Press,

Oxford), pp.1–38.

**Table S7. Rietveld refinement parameters for the experiment using $SiO_2$-coated α"-$Fe_{16}N_2$ sample at 423 K under $H_2$[a] (Experiment G).**

| Run# | *t* [hr] | $R_{exp}$[c] | $R_{wp}$[d] | S[e] | α"-$Fe_{16}N_2$ | | | α-Fe | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | *a* [Å] | *c* [Å] | $w_{Fe16N2}$[f] | *a* [Å] | $w_{Fe}$[g] |
| 0[b] | 0 | 2.68 | 3.78 | 1.41 | 5.71344(26) | 6.29021(44) | 0.986 | 2.86931(59) | 0.014 |
| 1 | 0.30 | 2.64 | 4.08 | 1.55 | 5.71379(34) | 6.30379(57) | 0.988 | 2.86916(99) | 0.012 |
| 2 | 1.54 | 2.65 | 3.96 | 1.49 | 5.71278(35) | 6.30478(60) | 0.990 | 2.8686(13) | 0.010 |
| 3 | 2.89 | 2.65 | 3.96 | 1.49 | 5.71243(36) | 6.30501(62) | 0.990 | 2.8716(17) | 0.010 |
| 4 | 4.24 | 2.65 | 3.93 | 1.48 | 5.71160(35) | 6.30421(61) | 0.990 | 2.8689(15) | 0.010 |
| 5 | 5.59 | 2.65 | 4.12 | 1.55 | 5.71141(38) | 6.30397(67) | 0.989 | 2.8668(13) | 0.011 |
| 6 | 6.94 | 2.65 | 4.10 | 1.55 | 5.71158(39) | 6.30467(68) | 0.990 | 2.8668(13) | 0.010 |
| 7 | 8.29 | 2.65 | 4.09 | 1.54 | 5.71123(38) | 6.30460(68) | 0.987 | 2.8686(17) | 0.013 |
| 8 | 9.64 | 2.65 | 4.11 | 1.55 | 5.71188(39) | 6.30445(69) | 0.988 | 2.8657(12) | 0.012 |
| 9 | 10.99 | 2.65 | 3.95 | 1.49 | 5.71172(38) | 6.30466(67) | 0.985 | 2.8696(16) | 0.015 |

a) 50 $cm^3$/min $H_2$

b) Rietveld refinement parameters of the sample determined before the $H_2$-treatment. Please see the Experimental Section in the Supporting Information for details.

c) expected profile R factor

d) weighted profile R-factor

e) $S = R_{wp}/R_{exp}$

f) relative weight fraction of α"-$Fe_{16}N_2$

g) relative weight fraction of α-Fe

For details of the $R_{exp}$ and $R_{wp}$;

Young, R. A. (**1993**). “Introduction to the Rietveld method,” *The Rietveld Method*, edited by R. A. Young, (Oxford University Press, Oxford), pp.1–38.

**Table S8: Average crystallite size, CS, of the α"- $Fe_{16}N_2$ samples before the $H_2$-treatment estimated by using the Scherrer formula.**

| Experiment | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| **CS [nm]** | 34.9 | 34.3 | 32.2 | 34.8 | 35.6 | 35.4 | 28.2 |