Nitrogen Absorption and Desorption Characteristics for $CeFe_7$

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Reversible nitrogen absorption and desorption cycle of $CeFe_7$ and Ce_2Fe_{17} was performed by heating in NH_3 or N_2 for nitrogenation and in H_2 for denitrogenation. The nitrogen absorption and desorption rates for $CeFe_7$ were faster than that for Ce_2Fe_{17} owing to the high diffusion rate of nitrogen for $CeFe_7$, resulting that the nitrogen absorption and desorption property of $CeFe_7$ was superior to that of Ce_2Fe_{17}.

It has been found that iron-based intermetallic compounds such as RE_2Fe_{17}, $TMFe_2$ (RE=rare earths, TM=transition metals) can reversibly absorb and desorb nitrogen via the formation of interstitial-type metal nitrides in a similar manner as hydrogen in the metal hydrides such as $LaNi_5$.[1–3] The nitrogen desorbed from their lattices easily reacts with hydrogen to generate ammonia in about 100% of yield because the nitrogen in the metal nitrides exists as an atomic state and is highly reactive in a manner similar to the hydrogen in the interstitial-type metal hydrides.[4,5]

In this work, the nitrogen absorption and desorption properties for $CeFe_7$ and Ce_2Fe_{17} were characterized. Both compounds belong to the Th_2Zn_{17}-type ones with space group of $R\bar{3}m$.[6] It is noted that Fe (6*c*) sites are fully occupied (occ=1) in the unit cell for Ce_2Fe_{17}, whereas Fe (6*c*) sites are partially deficient (occ=2/3) and Ce atoms occupy at 3*a* sites (occ=1/3) for $CeFe_7$. Therefore, $CeFe_7$ is regarded as iron-deficient Ce_2Fe_{17} compound, so that nitrogen would diffuse more readily in the bulk of $CeFe_7$ than that of Ce_2Fe_{17}. The differences of nitrogen absorption and desorption properties between $CeFe_7$ and Ce_2Fe_{17} are discussed from the viewpoint of the activation energy for nitrogen diffusion in their bulk.

The preparation of $CeFe_7$ and Ce_2Fe_{17} were made by the conventional arc melting method. The ingots obtained were annealed in He at 1073 K for 48 h, and then ground into powders with diameters below 50 μm. The samples prepared were checked by XRD. The respective surface area values of $CeFe_7$ and Ce_2Fe_{17} were 0.22 and 0.25 $m^2\ g^{-1}$. Each powder of $CeFe_7$ or Ce_2Fe_{17} (1 g) was charged in fixed-bed quartz tube and nitrogenated at 573–773 K for 1–3 h in NH_3 or N_2 with a flow rate of 30 mL min^{-1}. The hydrogenation (denitrogenation) was subsequently carried out at 523–723 K for 1–3 h in H_2 with the same rate as NH_3 or N_2. Nitrogen contents of the resulting metal nitrides were determined by a nitrogen/oxygen analysis. Amounts of the nitrogen desorption were evaluated from the difference of nitrogen contents before and after the denitrogenation. Nitrogen species in the denitrogenation were characterized on mass spectrometry. The catalytic activity of ammonia decomposition over $CeFe_7$ and Ce_2Fe_{17} was measured by gas chromatograph. The NH_3–He mixed gas (5 vol % of NH_3) was flowed with a rate of 20 mL $min^{-1}\ g^{-1}$. The conversion from NH_3 to N_2 and H_2 was calculated by integrating their peak areas.

The XRD pattern of $CeFe_7$ was mainly assigned to the Th_2Zn_{17}-type structure, but some weak peaks derived from $CeFe_2$ phase were also observed owing to the peritectical reaction between $CeFe_2$ and $CeFe_7$ during the cooling step. On the other hand, Ce_2Fe_{17} was obtained as a single phase of Th_2Zn_{17}-type compound. The nitrogenation reactions for $CeFe_7$ and Ce_2Fe_{17} were performed in NH_3 at 623 K for 1 h. The nitrogen contents per formula unit for $CeFe_7$ and Ce_2Fe_{17} after nitrogenation were 2.97 and 4.19, respectively. The nitrogen content per metal (N/M) for $CeFe_7$ was 0.37 (=2.97N/[Ce+7Fe]), which is higher than that for Ce_2Fe_{17} (N/M=0.22). After the subsequent denitrogenation for each metal nitride in H_2 at 723 K for 1 h, the respective amounts of the nitrogen desorbed per the chemical formula units for $CeFe_7$ and Ce_2Fe_{17} were 1.57 and 1.95 (ΔN/M=0.20 and 0.10). The usable amounts of nitrogen through the absorption and desorption from 1cm^3 of $CeFe_7$ (ρ = 7.97 g) and Ce_2Fe_{17} (ρ = 7.71 g) were 285 and 152 cm^3 converted as N_2 at 273 K and 0.1 MPa, respectively. These values were higher than that of high-pressure N_2 cylinder stuffed at 15 MPa at 298 K; the amount of nitrogen stored per 1cm^3 of it is calculated to be 137 cm^3. Additionally, it was found from the measurement of dependency of nitrogenation time for nitrogen concentration that nitrogenation of 673 K for 1 h attained the saturation of nitrogen absorption for $CeFe_7$ and Ce_2Fe_{17}. The respective usable amount of nitrogen (N_2) per 1 cm^3 of $CeFe_7$ and Ce_2Fe_{17} were 405 and 356 cm^3 (Table 1). The nitrogen storage ability of $CeFe_7$ is highest among the materials studied in our previous works.[1–3]

Table 1. Nitrogen storage abilities of $CeFe_7$ and Ce_2Fe_{17}

Materials	Nitrogen contents / x		Usable amount of N_2 / cm^3 [a]
	After nitrogenation	After denitrogenation	
Nitrogenation in NH_3 at 623 K for 1 h			
$CeFe_7N_x$	2.97	1.57 [b]	285
$Ce_2Fe_{17}N_x$	4.19	1.95 [b]	152
Nitrogenation in NH_3 at 673 K for 1 h			
$CeFe_7N_x$	4.32	2.10 [b]	405
$Ce_2Fe_{17}N_x$	8.86	4.28 [b]	356
Nitrogenation in N_2 at 773 K for 3 h			
$CeFe_7N_x$	1.31	1.21 [c]	18.5
N_2 cylinder	—	—	137
$TiFe_2N_x$ [d]	1.57	0.99	278

[a] The usable amounts of nitrogen were represented as the amounts of N_2 generated from the materials per unit volume (1 cm^3).
[b] Denitrogenation in H_2 at 723 K for 1 h.
[c] Denitrogenation in H_2 at 723 K for 3 h.
[d] Nitrogenation in NH_3 at 723 K for 3 h and denitrogenation in H_2 at 723 K for 3 h.

The mass spectrometry of the gaseous product in the denitrogenation for $CeFe_7N_x$ demonstrated that the nitrogen released from the metal nitride reacts with hydrogen to generate ammonia. Further, the amounts of ammonia product determined by monitoring the pH values of H_2SO_4 solution trap before and after the denitrogenation fairly agreed with the results as directly determined by their nitrogen analyses. These facts mean that the atomic nitrogen liberated from the crystal lattice is converted to ammonia in about 100% of yield.

The activity of ammonia decomposition over $CeFe_7$ and Ce_2Fe_{17} was measured by gas chromatograph. The conversion of ammonia decomposition at 573 K attained 90 % for $CeFe_7$, while 67 % for Ce_2Fe_{17}. The activity of ammonia decomposition over $CeFe_7$ was higher than that over Ce_2Fe_{17}. Activation energy values of nitrogen diffusion in the grain of $CeFe_7$ and Ce_2Fe_{17} were estimated from the model proposed by Uchida et al.[7] Measurements of the nitrogen desorption rates for $CeFe_7N_{3.0}$ and $Ce_2Fe_{17}N_{7.54}$ resulted in the activation energy values of nitrogen diffusion for $CeFe_7$ and Ce_2Fe_{17} to be 69 and 102 kJ/mol, respectively (Figure 1). From the viewpoint of crystal structure for both compounds, Fe(6*c*), Ce(6*c*), and Ce(3*a*) sites are aligned to *c*-axis with their respective coordinates (*z*) of 0.103, 0.340, and 0 as a hexagonal unit.[8] Since the Fe(6*c*) sites are fully occupied for Ce_2Fe_{17}, the nearest neighbor distance for Fe(6*c*)–Ce(6*c*) is calculated to be 0.294 nm. Meanwhile, the Fe(6*c*) sites are partially deficient and Ce occupies at 3*a* sites for $CeFe_7$, resulting that the nearest neighbor distance for Ce(3*a*)–Ce(6*c*) is 0.421 nm. The interatomic distance of 0.127 nm for Fe(6*c*)–Ce(3*a*) is too short to form such bonding. Therefore, the packing density along the *c*-axis for $CeFe_7$ is lower than that for Ce_2Fe_{17}. Nitrogen would diffuse more readily in $CeFe_7$ than Ce_2Fe_{17}. It is considered that the nitrogen absorption proceeds through the dissociation of ammonia molecules and the successive diffusion into the bulk for atomic nitrogen adsorbed on the surface. The excellent property of nitrogen absorption and desorption over $CeFe_7$ is ascribable to the high catalytic activity of ammonia decomposition over it and the ease of nitrogen diffusion in the bulk. In addition, the high nitrogen storage ability of $CeFe_7$ is attributable to the richer atomic concentration of Ce for $CeFe_7$ (12.5 at %) than that for Ce_2Fe_{17} (10.5 at %) due to the large standard enthalpy of formation for CeN (~320 kJ/mol).

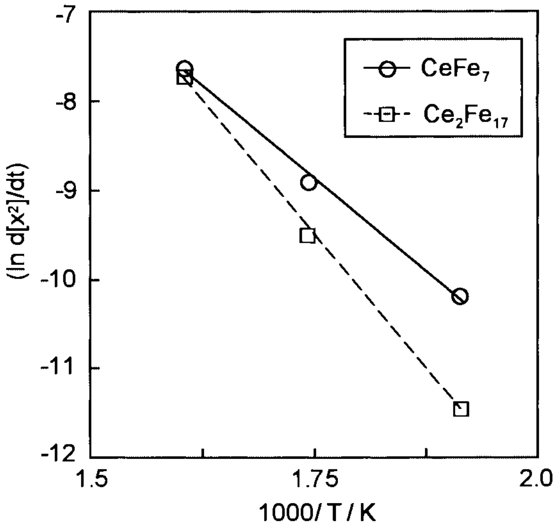

Figure 1. Arrhenius plots of the nitrogen desorption rate of $CeFe_7$ and Ce_2Fe_{17}.

The nitrogenation for $CeFe_7$ was conducted by heating in N_2 at 773 K for 3 h. The nitrogen content per chemical formula was 1.31 after nitrogenation. The following nitrogen desorption reaction was carried out in H_2 at 723 K for 3 h to desorb nitrogen down to $CeFe_7N_{1.21}$. The amount of nitrogen regenerated per 1 cm^3 of $CeFe_7$ was 18.5 cm^3 that sharply decreased compared with the case of nitrogenation in NH_3 (Table 1). The respective bond energy values of N–H in NH_3 and N≡N are 431 and 941 kJ mol^{-1}. The dissociation of strong triple bond of N_2 is considered to be a rate-determining step for nitrogen absorption reaction. The generating nitrogen species in the denitrogenation was detected to be ammonia from the mass spectrometry. The resulting amount of ammonia product per 1 g of $CeFe_7$ was 210 μmol. The above nitrogen absorption and desorption cycle is regarded as a novel nitrogenation process of hydrogen by fixing nitrogen from N_2 through the formation of interstitial-type metal nitride, since the highly reactive atomic nitrogen in the crystal lattice easily reacts with hydrogen to generate ammonia in about 100 % of yield.

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8 The atomic positions for Ce and Fe are referred from $PrFe_7$ in ref 6. The Crystal structures for $CeFe_7$ and $PrFe_7$ belong to Th_2Zn_{17}-type compound. Their XRD patterns are quite similar and are indexed by the same Miller number for respective diffraction peaks.