Formation and Hydrogenation of the Nitrogen Stored in Iron-based Intermetallic Compounds

Ken-ichi Machida,* Masahiro Ito, Kazuhiro Hirose, and Gin-ya Adachi*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka 2-1, Suita, Osaka 565-0871

(Received July 29, 1998; CL-980575)

From a study on nitrogenation and hydrogenation characteristics of Laves phase-type intermetallic compound ($TiFe_2$) and its surface modified composite ($Ru/Al_2O_3/TiFe_2$), nitrogen molecule was found to be converted to ammonia via formation of $TiFe_2N_x$ at ambient pressure.

A series of rare earth intermetallic compounds (R_2Fe_{17}) provide interstitial metal nitrides ($R_2Fe_{17}N_x$),[1,2] as well as metal hydrides, in which the atomic nitrogen is partly released from the crystal lattices by heating in Ar.[3] Meanwhile, Laves phase-type intermetallic compounds, M'M"$_2$ (M'=Ti and Zr; M"=V, Cr, Mn, and Ni), also interstitially absorb significant amounts of H_2 to form the corresponding metal hydrides such as M'M"$_2$H$_x$.[4] In this paper, nitrogenation and hydrogenation of $TiFe_2$ were made to study the absorption-desorption property of nitrogen via formation of the metal nitride.

The Laves phase-type intermetallic compound $TiFe_2$ was prepared from an appropriate amount of Ti (>99.9%) and Fe rods (>99.95%) on an arc melting apparatus, and ground to a particle size below 50 μm, after annealing in He at 1373 K, as well as TiFe. A part of the $TiFe_2$ powder was impregnated with $Al(C_2H_5)_3$ and $Ru_3(CO)_{12}$ solutions as precursors to prepared $Ru/Al_2O_3/TiFe_2$ composite powders by subsequent treatments: oxidation in air at room temperature for Al_2O_3 and reduction in H_2 at 673 K for Ru metal, according to methods.[5,6] Surface area of them was measured using to a conventional BET method, together with Ti (>99.0%) and Fe (>99.9%) powders: $TiFe_2$, TiFe, and $Ru/Al_2O_3/TiFe_2$, 0.15-0.30 m^{2}g^{-1}; Ti, 0.05 m^{2}g^{-1}; Fe, 0.17 m^{2}g^{-1}.

The $TiFe_2$, TiFe, Ti, and Fe powders (1.0 g) was individually charged in conventional fixed-bed quartz tube reactors (12 mm o.d.), and nitrogenated at 723 or 773 K in a stream of NH_3-H_2 mixed gas (molar ratio=1 : 1) or N_2 at a space velocity (SV) of 4000 h^{-1}, followed by a subsequent hydrogenation in H_2 under the same SV condition at 723 K. Nitrogen amounts regenerated from the metal nitrides were evaluated from differences between the nitrogen contents of nitrogenated and hydrogenated powders, which were measured on a nitrogen/oxygen analyzer (Horiba, EMGA 550). Structural modifications were checked by X-ray diffraction (XRD) patterns (CuKα radiation). Nitrogen species eluted from the metal nitrides during the hydrogenation were analyzed on a mass spectrometer, and the resulting ammonia was determined by monitoring a pH value of H_2SO_4 aqueous solution in a glass trap for the H_2 elution gas every the nitrogen absorption-desorption cycle.

Figure 1 shows XRD patterns of $TiFe_2$ and $TiFe_2N_x$ heated in the NH_3-H_2 mixed gas or H_2 at 723 K, respectively. The XRD patttern of $TiFe_2$ was completely assigned to the Laves phase-type structure (C14, hexagonal, $P6_3/mmc$),[7a] but the crystal lattice was transformed to an amorphous one by the nitrogenation. Also, Fe partly converted to an interstitial compound as assigned to Fe_3N.[7b] However, TiFe and Ti never showed such modification and, furthermore, the nitrogenation in N_2 at 773 K, no structural modification was observed even on $TiFe_2$ and Fe.

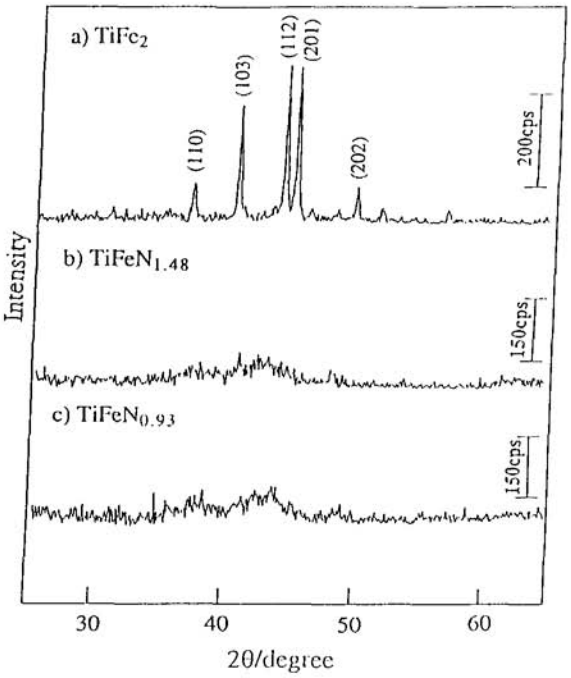

Figure 1. XRD patterns for the $TiFe_2$ and $TiFe_2N_x$ powders: a) as obtained; b) nitrogenated in the NH_3-H_2 mixed gas for 3 h at 723 K; c) hydrogenated in H_2 for 3h at 723 K.

Since the nitrogen species eluted by H_2 was completely assigned to NH_3 from mass spectrum signals, most of the nitrogen stored in the crystal lattices as metal nitrides was concluded to generate NH_3. Nitrogenation and hydrogenation (nitrogen absorption-desorption) properties of $TiFe_2$, TiFe, Ti, and Fe powders in the streams of NH_3-H_2 mixed gas or N_2 and H_2 were summarized in Table 1. It is noted that the amounts of ammonia calculated based on the compositional analysis values of the nitrogenated and hydrogenated powders of $TiFe_2$ (26.3 mmol cm^{-3}) are larger than a calculated one for a high-pressure (15MPa) nitrogen container (12.2 mmol cm^{-3}), where these mole values express the amounts of ammonia generated from 1.0 cm^3 of the metal nitride or the nitrogen container. The capacity to generate ammonia was still maintained at the high level even after 11th cycle (26.6 mmol cm^{-3}).

However, TiFe hardly absorbed nitrogen and the amount of resulting ammonia was only 3.13 mmol cm^{-3}, although hydrogen is efficiently absorbed in the crystal lattice.[8] Also, the nitrogen

Table 1. Nitrogen absorption-desorption characteristics of $TiFe_2N_x$, TiN_x, FeN_x, and $Ru/Al_2O_3/a\text{-}TiFe_2N_x$

Metal nitrides	Cycle number	Nitrogen content (x)		Generated ammonia[a] (mmol cm^{-3}(M.N.))
		Nitrogenated	hydrogenated	
(A) Nitrogenation in the NH_3-H_2 mixed gas at 723 K for 3 h				
$TiFe_2N_x$	1	1.48	0.93	26.3
	11	1.50	0.94	26.6
$TiFeN_x$	1	0.06	0.01	3.13
TiN_x	1	0.073	0.072	0.10
FeN_x	1	0.14	0.01	18.4
(B) Nitrogenation in N_2 at 773 K for 3 h				
$Ru/Al_2O_3/$ a-$TiFe_2N_x$	1	1.57	1.51	2.57
	2	1.60	1.55	2.14
	5	1.72	1.67	2.14

[a] Calculated per 1.0 cm^3 of metal nitrides from their compositional analysis values. The NH_3 amount generated from 1.0 cm^3 of nitrogen container charged at 15 MPa is evaluated to be 12.2 mmol cm^{-3} if the N_2 gas might be converted to NH_3 at 100% of yield.

storage capacity of Ti was negligible, but the Fe powder absorbed a significant amount of nitrogen as Fe_3N, providing 18.4 mmol cm^{-3} of ammonia, although the generated ammonia from Fe_3N was still less than those from $TiFe_2N_x$. This good nitrogen capacity is due to the formation of interstitial metal nitrides Fe_3N in a similar manner as the rare earth-iron metal nitrides such as $R_2Fe_{17}N_x$.[9]

On the other hand, the nitrogenation using N_2 scarcely took place even on $TiFe_2$. However, once the $TiFe_2$ powder was coated with a Ru/Al_2O_3 catalyst and preliminary nitrogenated in the NH_3-H_2 mixed gas to transform to the amorphous phase (a-$TiFe_2$), nitrogen was reversively absorbed and desorbed over the Ru/Al_2O_3/a-$TiFe_2$ composite powder by heating in N_2 and H_2, resulting in 2.57 mmol cm^{-3} of NH_3, although the amount was considerably small compared with the value observed in the cycle of NH_3-H_2 mixed gas and H_2. The determined amount of NH_3 fairly agreed with a value calculated from the nitrogen content of metal nitrides (see Table 2). The considerable decrease in the ammonia amount is due to the partial oxidation of $TiFe_2$ itself in the process to form Al_2O_3 from $Al(C_2H_5)_3$ in air. The oxygen content was ~0.2 wt% for $TiFe_2$, but ~2.4 wt% for Ru(0.02 wt%)/Al_2O_3(~1.5 wt%)/$TiFe_2$).

Table 2. Determination of the ammonia generated from the $Ru/Al_2O_3/a\text{-}TiFe_2N_x$ composite powder at the 2th cycle as shown in Table 1

Analysis	Nitrogenation[a]		Generated ammonia[b] (mmol cm^{-3}(M.N.))
	Before	After	
pH value[a] (aq.H_2SO_4)	3.03	8.01	2.23

[a] Measured on the H_2SO_4 aqueous solutions before and after introducing the H_2 elution gas from the metal nitride. [b] Evaluated from changes of pH and x values.

In conclusion, the amorphous interstitial metal nitride, a-$TiFe_2N_x$, is responsible for the high capacity to regenerate NH_3, nitrogen molecule is fixed in the $Ru/Al_2O_3/TiFe_2$ composite material even at ambient pressure.

This work was partly supported by Grant-in-Aid for Scientific Research Nos. 07242245, 08232249, 09218234, and 09874143 from the Ministry of Education, Science, Sports, and Culture of Japan.

References and Notes

1 J. M. D.Coey and H. Sun, *J. Magn. Magn. Mater.*, **87**, L251 (1990).
2 T. Iriyama, K. Kobayashi, and H. Imai, European Patent, 0-369-097-A1 (1989).
3 T. Iriyama, T. Katsumata, and R. Mitsui, *Trans. Mat. Res. Soc. Jpn.*, **14B**, 1063 (1994).
4 "Hydrogen in Intermetallic Compounds I and II," in "Topics in Applied Physics," ed by L. Schlapbach, Springer-Verlag, Tokyo (1992), Vol. 67.
5 Y. Kadowaki and K. Aika, *J. Catal.*, **161**, 178 (1996).
6 C. C. Nagel, J. C. Bricker, D. G. Alway, and S. G. Shore, *J. Organomet. Chem.*, **219**, C9 (1981).
7 "Binary Alloy Phase Diagrams," ed by T. B. Massalski, J. L. Murray, L. H. Bennett, and H. Baker, Amer. Soc. Met., Metals Park (1986), Vol. 1, a) $TiFe_2$, pp.1117-1119; b) Fe_3N. pp.1079-1083.
8 L. Zaluski, S. Hosatle, P. Tessier, D. H. Ryan, J. O. Ström-Olsen, M. L. Trudeau, and R. Schultz, *Z. Phys. Chem.*, **183**, 45 (1994).
9 K. Machida, K. Hirose, H. Nakajima, and G. Adachi, to be published.