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Preparation of CeN by reaction of Ce with a N_2–H_2 mixture

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Abstract

It has been found that although the reaction of Ce with N_2 does not proceed at 200–300 °C at an appreciable rate, the use of a gaseous mixture of N_2 and H_2 makes the formation of cerium mononitride (CeN) possible at these low temperatures. Preliminary experimental results of the reaction, $Ce + (N_2 + H_2)$, together with those for $Ce + H_2$, $Ce + N_2$ and $CeH_{3-x} + N_2$ are reported.

1. Introduction

One common method for preparing metal nitrides is to use the reaction of a metal with N_2. But a mixture of N_2 and H_2 is often used as a nitriding agent instead of N_2. Although, in some cases, the addition of H_2 to N_2 seems to be indispensable for facilitating the nitride formation, the role of H_2 has not yet been well understood. If the metal has no tendency to form a nitride but a strong tendency to form a hydride, the mixture of N_2 and H_2 may act as a hydriding agent. When the conditions are such that the formation of nitride may occur in parallel with the hydride formation, the two reactions competing with each other, the situation may be further complicated. In order to gain some insights into the role of hydrogen in nitride formation by the reaction of metals with a mixture of N_2 and H_2, the reaction experiments of Ce metal with gaseous mixtures of N_2 and H_2 were carried out at temperatures of 200–300 °C. For comparison, the reaction of Ce with N_2 and that with H_2 were performed. Also, the reaction of Ce hydride with N_2 was carried out at 250 °C.

It has been long accepted that CeH_2 with a fcc coordination of the cerium atoms takes up further hydrogen forming the isomorphic CeH_3 and that a continuous solid solution exists in the CeH_2–CeH_3 range. The variation in the lattice parameter, *a*, of the hydride with hydrogen content has been reported by several workers [1–5]. However, Kaldis *et al.* [6] claimed that there exists a wide field of the tetragonal distortion in the range ($2.28 < H{:}Ce < 2.65$) with various degrees of hexagonal splittings. Since the main aim of this work is to explore, at least qualitatively, the role of hydrogen in CeN formation by the reaction of Ce with N_2/H_2 mixtures, this non-stoichiometric cerium hydride is written as CeH_{3-x} hereafter. Heat capacity and thermodynamic functions of CeH_2 have been given by Stalinski and Bieganski [7]. Although the thermodynamic data for the formation of Ce mononitride (CeN) reported in the literature [8] may suggest that low reaction temperatures are favorable for CeN formation, temperatures higher than 800 °C will be required to prepare the nitride by the reaction of Ce metal with N_2 [9]. This indicates that although from an equilibrium point of view the reaction $Ce + 1/2N_2 = CeN$ should proceed to the right, the activation energy for the CeN formation is very high at temperatures of 400 °C or less. The range of non-stoichiometry of CeN may not be so wide but the existence of non-stoichiometric CeN cannot be excluded [8]. In this paper, this nitride is written as CeN_y.

2. Experimental details

About 1.6 g of a cerium metal rod (99.9% by supplier's claims) was leached in 10 N HNO_3 and washed in water and ethyl alcohol. A quartz boat containing the specimen was placed in the center of the reaction tube and the system was evacuated to the order of 10^{-6} Pa at room temperature. Then N_2 and H_2 were introduced to the reaction tube up to the respective predetermined partial pressures. After confirming the complete mixing of N_2 and H_2 at room temperature with a gas chromatograph (type GC-3BT, Shimadzu, Co. Ltd., Kyoto, Japan), the temperature was raised to the desired level. Variations in the partial pressures of N_2 and H_2, $P(N_2)$ and $P(H_2)$ were followed by means of gas chromatography measurements and the total pressure, *P*(Total) was also determined by a capacitance manometer. The X-ray diffraction powder patterns of the reaction products were obtained at room temperature with a diffracto-

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meter (Rigaku Denki; Geiger flex rad-rA) using crystal-monochromatized Cu Kα radiation.

3. Results and discussion

The experimental results are summarized in Table 1 and X-ray diffraction patterns for some of the reaction products are shown in Fig. 1. Peaks corresponding to CeN_y are observed in the diffraction patterns for the reaction products obtained by the $Ce+(N_2+H_2)$ reaction at 200 and 250 °C (see Fig. 1(a) and (b)). These broad peaks indicate that the crystallization of these CeN_y samples is poor. In the case of the reaction at 250 °C (run 2), a significant amount of the CeH_{3-x} phase is also present in the product (see Fig. 1(b)). At 200 °C (run 1), CeN_y with poorer crystallization is formed, while the hydride becomes the major phase (see Fig. 1(a)). On the other hand, the X-ray diffraction pattern of CeN_y formed by the reaction of Ce with the N_2/H_2 mixture at 300 °C (Fig. 1(c)) shows that the reaction product consists only of CeN_y, and the crystallization of the nitride is improved. As can be seen from Table 1, reactions of Ce with N_2/H_2 mixtures lead to the formation of CeN_y at such low temperatures as 200–300 °C although, in some cases, CeH_{3-x} co-exists. On the other hand, no reaction takes place between Ce and N_2 at these low temperatures (runs 6, 7). It has also be found that Ce metal reacts easily with H_2 to produce CeH_{3-x} at 200 (run 4) and 250 °C (run 5) (see also Fig. 1(d)). These results clearly show that the use of gaseous mixtures of N_2 and H_2 is more effective as a nitriding agent than N_2 alone.

Typical variation in P(Total), $P(N_2)$ and $P(H_2)$ with time are shown graphically in Figs. 2 and 3. When a Ce specimen is exposed to an atmosphere consisting of N_2 and H_2 at 250 °C or 300 °C, P(Total) and $P(H_2)$ first decrease rapidly and then, through the minima, both continue to increase while $P(N_2)$ decrease relatively slowly throughout the run. The rapid decrease of $P(H_2)$ observed in the early stage of the run may be ascribed to the formation of CeH_{3-x} according to $Ce+(3-x/2)H_2=CeH_{3-x}$ (the atomic ratio of H:Ce of the hydride estimated from the calculated lattice parameter values ranges from 2.3 to 2.4, according to the data given by Holley *et al.* [1]). The hydride may be gradually converted to CeN_y by the reaction $CeH_{3-x}+(y/2)N_2=CeN_y+(3-x/2)\ H_2$. However, the possibility cannot be ruled out that a mixed phase such as CeN_xH_{3-x} is first formed by the reaction of CeH_{3-x} with N_2 and then this mixed phase can continue to react with N_2 and lose H_2 as the reaction proceeds since the hydride formed in the early stage can accommodate nitrogen atoms to form a mixed phase.

The reaction of CeH_{3-x} with N_2 was also performed at 250 °C. The CeH_{3-x} sample was prepared in the same way as in run 5 and then N_2 was introduced into the system. It was found that as the reaction proceeds, CeH_{3-x} continues to react with N_2 and evolve H_2. The X-ray diffraction analysis shows the formation of CeN_y (see Fig. 1(e)).

The disruption of N_2 into 2N may be a prerequisite for the formation of CeN_y by the reaction of Ce with N_2. The present experimental findings that no reaction occurs between Ce and N_2 at 300 °C or less may suggest

TABLE 1. Experimental results of reactions: $Ce+(N_2+H_2)$, $Ce+H_2$, $Ce+N_2$, and $CeH_{3-x}+N_2$

Run	Reactants	Initial pressures of gas reactants (kPa)		Final pressures of gas reactants (kPa)		Reaction temperature (°C)	Reaction time (h)	Identified solid phases and their lattice parameter (nm)	
		$P(N_2)$	$P(H_2)$	$P(N_2)$	$P(H_2)$				
1	$Ce+(N_2+H_2)$	16	48	27	14	200	60	CeN_y (0.5015)	$+CeH_{3-x}$ (0.5539)
2	$Ce+(N_2+H_2)$	17	51	45	8	250	60	CeN_y (0.5022)	$+CeH_{3-x}$ (0.5552)
3	$Ce+(N_2+H_2)$	17	47	6	49	300	40	CeN_y (0.5023)	
4	$Ce+H_2$	0	67	0	40	200	5		CeH_{3-x} (0.5570)
5	$Ce+H_2$	0	16	0	0	250	1		CeH_{3-x}[a] (0.5577)
6	$Ce+N_2$	48	0	48	0	250	66	Ce (no reaction occurred)	
7	$Ce+N_2$	80	0	80	0	300	103	Ce (no reaction occurred)	
8	$CeH_{3-x}+N_2$	48	0	35	16	250	40	CeN_y (0.5019)	

[a] The solid product includes metallic Ce in addition to CeH_{3-x}.

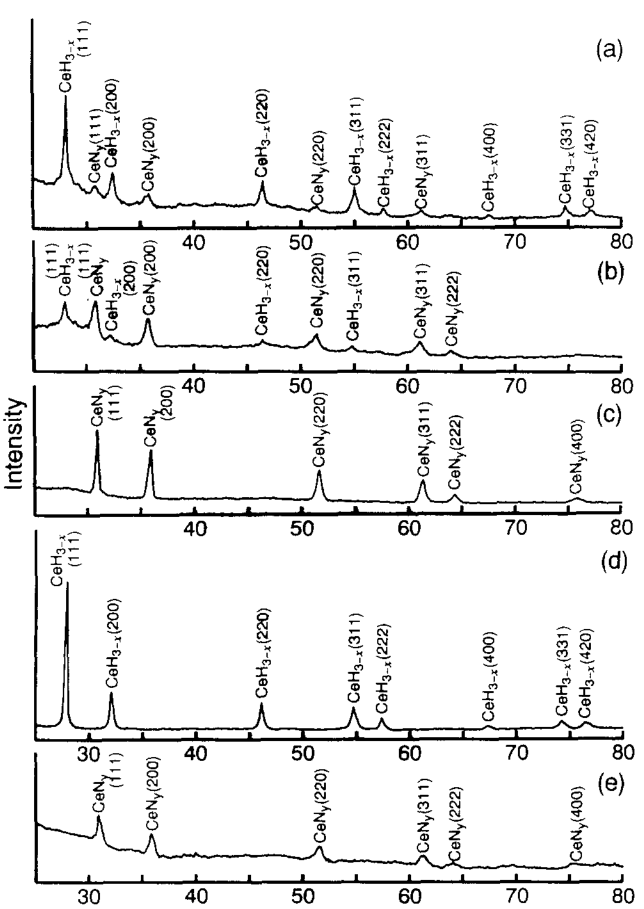

Fig. 1. X-Ray diffraction patterns of products of the reactions: (a) Ce with N_2/H_2 mixture (N_2:H_2=1:3) at 200 °C; (b) Ce with N_2/H_2 mixture (N_2:H_2=1:3) at 250 °C; (c) Ce with N_2/H_2 mixture (N_2:H_2=1:3) at 300 °C; (d) Ce with H_2 at 250 °C; (e) CeH_{3-x} with N_2 at 250 °C.

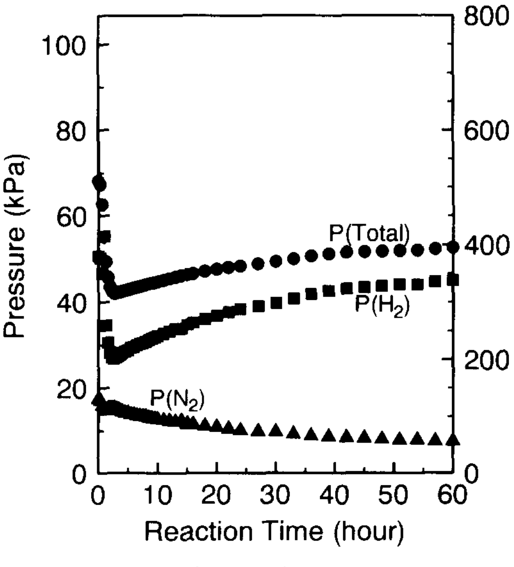

Fig. 2. Time variation of P(Total), $P(N_2)$ and $P(H_2)$ during the reaction of Ce with N_2/H_2 mixture (N_2:H_2=1:3) at 250 °C.

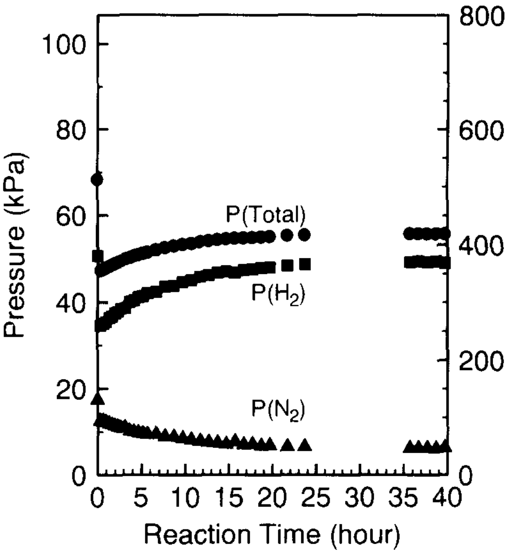

Fig. 3. Time variation of P(Total), $P(N_2)$ and $P(H_2)$ during the reaction of Ce with N_2/H_2 mixture (N_2:H_2=1:3) at 300 °C.

that these low temperatures are not sufficiently high for this purpose. On the other hand, the addition of H_2 to N_2 makes the formation of CeN_y possible at such low temperatures. It is highly likely that CeN_y has been obtained through the reaction of CeH_{3-x} with N_2, suggesting that CeH_{3-x} plays an important role in disrupting $N\equiv N$ bond.

Even under conditions where the formation of CeN_y may be more favorable than the formation of CeH_{3-x} from the equilibrium thermodynamic point of view, the reactants of Ce, N_2 and H_2 can produce CeH_{3-x} in the early stage of the reaction. Thus, in this stage, the hydride formation reaction seems to proceed much faster than the nitride formation reaction and then the once formed CeH_{3-x} is being converted to CeN_y, either *via* a mixed phase CeN_xH_{3-x} or directly. CeH_{3-x} may be in equilibrium with the gaseous mixture of N_2 and H_2 for a short period of time or even instantaneously before the final equilibrium is reached between CeN_y and the gas phase.

3. Concluding remarks

It is well known that NH_3 acts as a more effective nitriding agent than N_2. Thus, when it is difficult to prepare metal nitrides by reaction of metal or metal hydride with N_2, either NH_3 or a gaseous mixture of N_2 and H_2 is often used. To explore the role of H_2 in the formation of metal nitrides by the reaction of metals with a N_2/H_2 mixture, experiments with Ce+(N_2+H_2) and CeH_{3-x} with N_2 were performed. When metallic cerium is exposed to N_2 under normal pressures at 200–300 °C, no reaction occurs. On the other hand, if gaseous mixtures of N_2 and H_2 are employed instead of N_2, CeH_{3-x} is first formed and then CeN_y is obtained by the reaction of the CeH_{3-x} with N_2. It is clear from the present work that the presence of hydrogen as H_2 in the gas phase or in the form of CeH_{3-x} is necessary to disrupt N≡N bonding at such low temperatures as 200–300 °C.

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