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Reaction of Ce with NH_3

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Abstract

In order to examine the nitriding ability of NH_3, the reactions of Ce with NH_3 and that of Ce with N_2 were performed at 250 °C. The former reaction can readily produce CeN while the latter does not proceed to any measurable extent. The results clearly show the superiority of NH_3 as a nitriding agent over N_2.

1. Introduction

It is known that cerium mononitride (CeN) can be prepared by the reaction of cerium metal or cerium hydride with N_2 or NH_3 at temperatures higher than 800 °C. Schumacher and Wallace [1] converted Ce hydride to CeN by the reaction with N_2 at 900–1000 °C for about 3 days, while Brown and Clark [2] prepared CeN by heating Ce in N_2 at 800–950 °C for 400 h. Vogt *et al.* [3] obtained CeN by nitridation of Ce at 900 °C under 1 atm of NH_3. However, little work on the preparation of the nitride has been reported at lower temperatures in the literature. Gaseous ammonia is more favorable as a nitriding agent than N_2 from both the kinetic and equilibrium points of view [4,5]. The following two kinetic merits are known for NH_3 gas as a nitriding agent: (1) the use of NH_3 makes the reaction period much shorter and (2) the nitride is formed at relatively low temperatures compared with the case where N_2 gas is used. It is well known that reactions of some metals (*e.g.* Fe, Mo or U) with a stream of NH_3 often result in the formation of nitrogen-rich metal nitrides [4,6,7], which cannot be obtained by N_2 at normal pressure. This fact strongly suggests that a stream of NH_3 may possess much higher nitrogen activity compared with that of nitrogen gas. Therefore, the nitrogen-rich nitride formation by the use of a stream of NH_3 must be considered from the equilibrium point of view. Thermodynamically unstable NH_3 gas can be prepared by maintaining its extent of dissociation in N_2 and H_2 well below the equilibrium dissociation degree at the temperature in question. During the course of our research on the formation of CeN, it has been found that at relatively low temperatures (400 °C or less), the decomposition of NH_3 can be suppressed almost completely by use of a quartz reaction vessel.

As part of a continuing effort to examine the nitriding ability of unstable NH_3, a relatively large amount of work on Ce + NH_3 has been carried out at temperatures lower than 400 °C in our laboratory. Although the main aim of this work is to examine the nitriding ability of NH_3 through the reaction Ce + static NH_3, it was also intended to enhance only the nitriding reaction by a proper choice of experimental conditions, especially temperature. This paper describes the experimental results for the reaction of Ce with static NH_3 at 250 °C. Variation in the total pressure P(Total) and in the partial pressure of NH_3, H_2, and N_2 ($P(NH_3)$, $P(H_2)$, and $P(N_2)$) with time are investigated. For comparison, the reaction of Ce with N_2 was also carried out at the same temperature.

2. Experimental details

2.1. Materials

Nominal impurities in an as-received rectangular-shaped cerium metal specimen ($4 \times 4 \times 15$ mm^3) are La < 100 ppm, Nd < 100 ppm, Fe < 70 ppm, Mg < 60 ppm and Ca < 20 ppm. The gases used in this work, NH_3 (99.998%) and N_2 (99.998%), were supplied from a commercial gas cylinder and were fed into the reaction system through a stainless steel capillary without further purification.

2.2. Procedure

A cerium specimen was leached in 10 N HNO_3 for a few seconds and washed with water. This treatment was repeated three times. Then it was weighed accurately. A quartz boat containing the pre-treated specimen was placed in the center of a quartz reaction tube and the system was evacuated to 4×10^{-6} Pa at room temperature. The ammonia gas was admitted into

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the reaction tube up to 67 kPa (500 Torr). After raising the temperature to 250 °C, the total pressure, P(Total) was measured with the help of a capacitance manometer (MKS BARATRON Type 122A, MKS Japan, Inc., which covered the pressure range 1.33×10–1.33×10^5 Pa with an accuracy of $\pm 0.5\%$), and the partial pressures, $P(NH_3)$ and $P(N_2)$ were determined with a gas chromatograph measurement (type GC-3BT, Shimadzu Co Ltd., Kyoto, Japan). The partial pressure of H_2, $P(H_2)$, was calculated by the relation of $P(H_2) = P(\text{Total}) - P(NH_3) - P(N_2)$, since $P(N_2)$ and $P(NH_3)$ could be much more accurately determined by the gas chromatograph measurement than $P(H_2)$. (The accuracy of the measurements of $P(N_2)$ and $P(NH_3)$ were ± 133 Pa and ± 200 Pa, and their respective detection limits were 40 Pa and 67 Pa.)

The X-ray diffraction powder pattern of the solid reaction product was obtained at room temperature with a diffractometer (Rigaku; Geiger flex rad-rA) using crystal monochromatized Cu Kα radiation. The solid product (CeN) was crushed in an agate mortar to fine powder and this powder was embedded in an Al sample holder with an epoxy resin to avoid possible oxidation of the specimen during X-ray diffraction. The above sample preparation was done under an Ar atmosphere.

3. Results and discussion

Cerium metal reacts easily with H_2 under normal pressure at temperatures of 200–350 °C to form CeH_3. It is known that cerium mononitride (CeN) exists in the Ce–N system. Thus, when a cerium metal specimen is brought into contact with NH_3, the following three reactions are possible:

$$Ce + NH_3(g) = CeN + 3/2H_2 \qquad (1)$$

$$Ce + NH_3(g) = CeH_3 + 1/2N_2 \qquad (2)$$

$$NH_3(g) = 1/2N_2 + 3/2H_2 \qquad (3)$$

where eqn. (3) represents the decomposition of NH_3 into N_2 and H_2 catalyzed by the surfaces of the Ce specimen. Under the condition that reaction (1) is predominant and reactions (2) and (3) are very slow or even imperceptible, NH_3 is being continuously consumed and H_2 is being continuously accumulated in the system. As a result, $P(NH_3)$ decreases and $P(H_2)$ increases in the course of the reaction and N_2 will never be present in the system. On the other hand, if only reaction (2) proceeds in a closed system, $P(NH_3)$ decreases and $P(N_2)$ increases continuously and H_2 will not exist in the system. If reaction (3), the decomposition of NH_3 prevails over reactions (1) and (2), both $P(H_2)$ and $P(N_2)$ continue to increase until the dissociation equilibrium is attained and, throughout the reaction, the ratio of $P(H_2)$ to $P(N_2)$ must be equal to 3. If two of the three reactions or all three reactions take place simultaneously, the pressure variation curves may exhibit rather complicated behavior.

The experimental result of the reaction of Ce with NH_3 is given in Fig. 1 where the time variations in P(Total), $P(NH_3)$, $P(H_2)$ and $P(N_2)$ are shown graphically. The pressure variation curves can be roughly divided into three regions, as shown in Fig. 1. Region I may be regarded as an induction period. As seen in Fig. 1, as the reaction proceeds, $P(NH_3)$ continues to decrease and $P(H_2)$ continues to increase in region II and eventually a saturated state (region III) is reached where there is no appreciable time dependence of $P(NH_3)$ and $P(H_2)$ being observed. It should be noted that, throughout the run, $P(N_2)$ was well below the detection limit (40 Pa = 0.3 Torr). Figure 2 shows the X-ray diffraction pattern of the solid phase cooled quickly to room temperature immediately after the termination of the run. The pattern consists only of the peaks corresponding to CeN. (A value of 0.5027 nm is obtained by Cohen's method for the lattice parameter

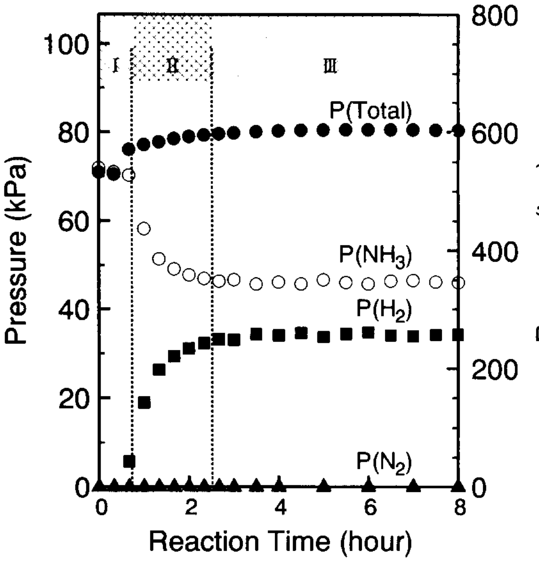

Fig. 1. Time variation of P(Total), $P(N_2)$, $P(H_2)$ and $P(NH_3)$ during the reaction of Ce with NH_3 at 250 °C.

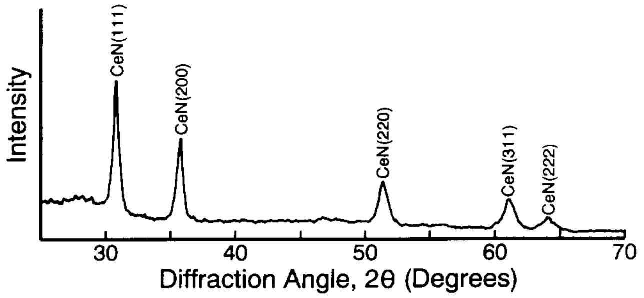

Fig. 2. X-Ray diffraction pattern of the reaction product.

of this CeN.) A crude check of the Ce:N ratio in the CeN obtained was made based on both the pressure drop of $P(NH_3)$ and the weight change of the solid specimen. A value of 1.08 for Ce:N was computed based on the former method and 1.10 was obtained from the latter. Although the existence of a non-stoichiometric CeN phase may not be inferred from these results, it is clear that the major phase of the solid is CeN. If only the direct nitriding reaction of Ce by NH_3, *i.e.* reaction (1) proceeds, the ratio of the increase in $P(H_2)$ to the decrease in $P(NH_3)$, $\Delta P(H_2)/(-\Delta P(NH_3))$, must be 1.5. A rough calculation shows this ratio to be about 1.45. Although the possibility of the formation of a very small amount of CeH_3 and that of a very small fraction of NH_3 decomposition cannot be ruled out, it may be concluded from the present experiment that reaction (1) is responsible for the pressure variations in Fig. 1 for the most part.

A cerium metal specimen was exposed to N_2 atmosphere at 48 kPa (360 Torr) at 250 °C for about 70 h. No decrease in $P(N_2)$ was observed and no CeN was formed, indicating that the reaction between Ce and N_2 at normal pressure does not proceed to any appreciable extent. This experimental result of the reaction of Ce with N_2 at 250 °C contrasts sharply with the reaction of Ce with static NH_3, which results in the formation of CeN within a relatively short period of time (about 2–3 h at 250 °C). Katsura [1] pointed out that thermodynamically unstable NH_3 prepared by suppressing its decomposition may possess an enormously high nitrogen activity compared with that of N_2 at 1 bar. Recently, Katsura *et al.* [2] have prepared uranium sesquinitride, U_2N_3 by the reaction of U with static NH_3 at 250 and 300 °C, at which temperatures U_2N_3 will never be formed by the reaction of U with N_2 at 1 bar. They have ascribed the formation of U_2N_3 by the action of static NH_3 to its high nitrogen activity arising from the thermodynamic instability. High nitrogen activity of NH_3 may also be responsible for the formation of CeN by the reaction of Ce with static NH_3.

The fact that no cerium hydride (CeH_{3-x}) has been observed in the final product does not exclude the possibility of CeH_{3-x} as an intermediate which facilitates the formation of CeN at such a low temperature as 250 °C.

4. Concluding remarks

Ammonia gas is a more favorable nitriding agent compared with N_2 from the kinetic point of view. When NH_3 is employed as a nitriding agent, the rate of formation of metal nitrides is considered to increase as the extent of instability of NH_3 is raised by keeping its decomposition well below the equilibrium dissociation. The present work on the reaction of Ce with static NH_3 at 250 °C clearly shows that CeN can be easily prepared by use of NH_3 instead of N_2 at such a low temperature as 250 °C.

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