ELSEVIER

Journal of Alloys and Compounds 418 (2006) 251–254

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Preparation and properties of nanocrystalline ytterbium and europium nitride (YbN and EuN)

H. Imamura*, Y. Sakata, T. Nuruyu, T. Imahashi

Department of Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan

Received 9 June 2005; received in revised form 9 August 2005; accepted 17 October 2005

Abstract

Nanocrystalline rare earth nitrides (EuN and YbN) were successfully prepared by the thermal decomposition of amides ($Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$). The formation processes of nanocrystalline nitrides were characterized by X-ray diffraction analysis (XRD) combined with temperature-programmed desorption (TPD) techniques. The amides were first decomposed to form imide with evolution of NH_3 and subsequently the conversion into nitride occurred. The surface areas increased markedly with increase in temperatures and went up to 146 $m^2 g^{-1}$ upon thermal decomposition of $Yb(NH_2)_2$ to YbN around 773 K, while EuN obtained by the thermal decomposition of $Eu(NH_2)_2$ at 573 K yielded surface areas of 107 $m^2 g^{-1}$. Such nanocrystalline YbN and EuN readily reacted with ammonia even at room temperature upon contact with ammonia (0–4.67 kPa). The properties of ammonia taken up by the nitride were evaluated by TPD and XRD. XRD of the NH_3-treated YbN showed diffraction peaks shifted to lower angles, indicating that the ammonia molecules entered the crystal lattice with the expansion of crystal constants.

Keywords: Chemical synthesis; X-ray diffraction; Thermal analysis; Nanostructures; Gas–solid reactions

1. Introduction

Recently, there has been a growing interest in science and application of rare earth materials. We have studied catalytic properties of a variety of rare earth compounds. In particular, by taking advantages of the solubility of europium and ytterbium metals in liquid ammonia [1], we have proposed the preparative methods of novel rare earth catalysts and have simultaneously demonstrated their unexpected catalysis for various reactions [2].

In this study, interest has centered on identifying the preparative conditions of nanocrystalline ytterbium and europium nitride (YbN and EuN) obtained by thermal decomposition of rare earth amides ($Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$). It has been shown elsewhere [3,4] that the catalytic activity of YbN and EuN for hydrogenation reactions is higher than expected. The formation processes of nanocrystalline nitrides were characterized by X-ray diffraction analysis (XRD), combined with temperature-programmed desorption (TPD) and surface area measurements. The physico-chemical properties of nanocrystalline YbN and EuN were further characterized.

2. Experimental

2.1. Procedures of sample preparation

Eu and Yb (99.9%) were obtained from Santoku Co. Ammonia gas (Iwatani Ind. Ltd.) was purified through a calcium oxide column and subsequently through a sodium hydroxide column.

The rare earth amides ($Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$) were prepared using liquid ammonia as follows [4]. In a 50 cm^3 stainless steel reactor were placed Eu or Yb metals (ca. 0.5 g) under an atmosphere of dry nitrogen. The reactor was briefly evacuated, cooled by a dry ice/methanol bath, and then, about 1350 cm^3 of purified ammonia gas was liquefied. The Eu and Yb metal readily dissolved in liquid ammonia to yield a homogeneous rare earth metal solution [1]. The solutions were allowed to stand at 273 K, resulting in the formation of amide products as a precipitate. Ammonia was subsequently removed from the reactor leaving powdery products. The thermal treatment of rare earth amides was subjected to evacuation at elevated temperatures for 1 h.

2.2. Characterization

XRD analyses of the amides and their decomposed products were conducted with a Rigaku X-ray diffractometer (RINT 2200) using Cu Kα radiation. TPD measurements were made in vacuo at a heating rate of 2.5 K min^{-1} by contin-

---

* Corresponding author. Tel.: +81 836 85 9680; fax: +81 836 85 9601.
E-mail address: hi-khm@yamaguchi-u.ac.jp (H. Imamura).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.10.074

uously monitoring desorbed gases via quadrupolar mass spectrometer. Surface areas were measured with a Shimadzu TriStar 3000. All procedures of the rare earth samples were carried out without exposure to air.

3. Results and discussion

3.1. Preparation of nanocrystalline YbN and EuN by thermal decomposition of amides

The use of amides ($Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$) consisting of stoichiometric structures as starting materials is an important factor in the preparation of the nitrides, EuN and YbN, respectively. It has been proved that $Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$ are nearly quantitatively prepared by controlling the reaction conditions of the Eu or Yb metals with liquid ammonia [4]. The thermal decomposition of the amides led to the preparation of the fully satisfactory nitrides in stoichiometry, which had often become a subject of discussion so far [5].

The nanocrystalline YbN with cubic structures was stoichiometrically obtained by the decomposition of the diamide $Yb(NH_2)_2$ and triamide $Yb(NH_2)_3$ when these amides were heated around 773 K. There were no chemical and structural differences in the product YbN based on differences between both the amide precursors. As shown in the XRD pattern (Fig. 1), the triamide $Yb(NH_2)_3$ decomposed to the cubic YbN upon heating around 773 K similarly to $Yb(NH_2)_2$ [4]. The amides were usually converted into the nitride via imide (YbNH) [6–8]; thus, thermal decomposition to the nitride occurred successively. According to TPD of $Yb(NH_2)_3$ (Fig. 2) combined with mass spectrometers, the evolution of H_2 resulting from the conversion of YbNH into YbN was observed from about 700 K.

$$\text{YbNH} \rightarrow \text{YbN} + \tfrac{1}{2}H_2$$

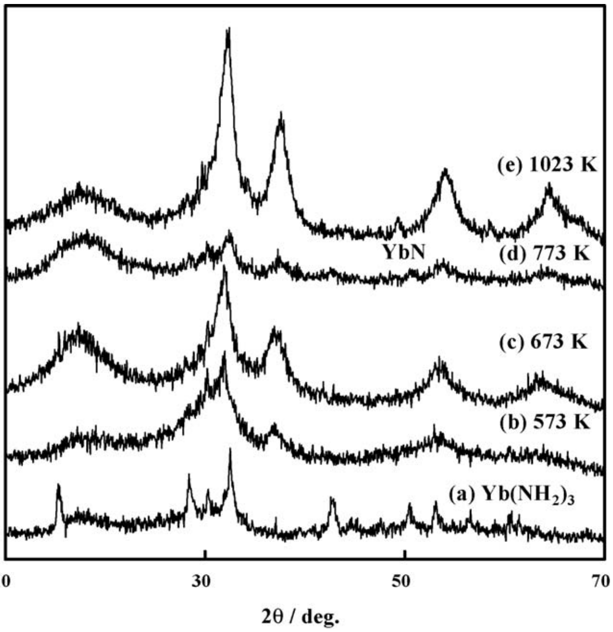

Fig. 1. Changes in XRD of $Yb(NH_2)_3$ with the thermal treatment. $Yb(NH_2)_3$ was subjected to evacuation for 1 h at the following temperatures: (a) as prepared, (b) 573 K, (c) 673 K, (d) 773 K and (e) 1023 K.

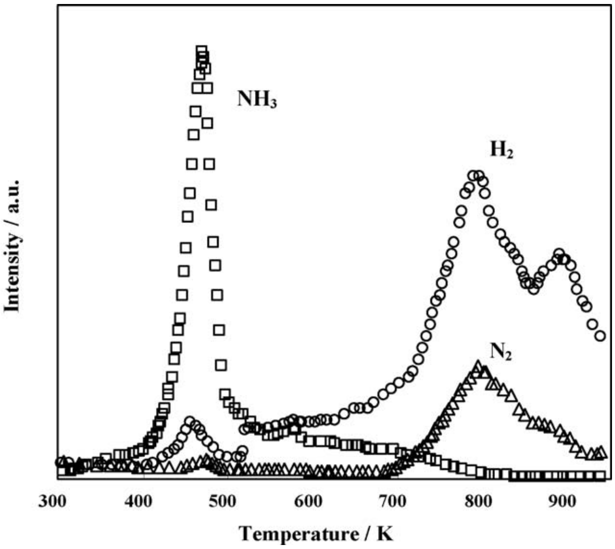

Fig. 2. TPD of $Yb(NH_2)_3$.

In Fig. 2, the evolution of N_2 observed in the range of about 700–900 K is probably due to further decomposition of YbN to YbN_{1-x}.

Judging from XRD and TPD recorded with the thermal treatment of $Eu(NH_2)_2$, the decomposition to EuN occurred similarly to the Yb amides. However, the decomposition temperatures to EuN were much lower, that is, 503–573 K.

During the thermal decomposition of the amides, the nanoparticles developed and the specific surface areas increased markedly with increase in evacuation temperatures. The surface areas went up to 144–146 $m^2\,g^{-1}$ upon decomposition of $Yb(NH_2)_2$ and $Yb(NH_2)_3$ to YbN around 773 K (Table 1). Further heating of YbN to 1023 K resulted in a decrease in surface area to 123–126 $m^2\,g^{-1}$. The crystallite sizes of YbN evacuated at 1023 K, which were evaluated by line broadening of the (1 1 1) diffraction peak, were 28 nm. The nanocrystalline EuN obtained by the thermal decomposition of $Eu(NH_2)_2$ at 573 K yielded surface areas of 107 $m^2\,g^{-1}$ (Table 1). However, EuN was liable to be sintered to a significant extent, compared to YbN. The surface areas of EuN obtained at 773 and 1023 K decreased to 49 and 1 $m^2\,g^{-1}$, respectively.

3.2. Properties of nanocrystalline YbN and EuN

Such nanosized rare earth nitrides readily reacted with ammonia within few minutes even at room temperature when brought into contact with ammonia gas (0–4.67 kPa). The reaction with ammonia was carried out using high-vacuum glass equipment with a fixed volume and the NH_3 uptake was monitored by the changes in pressures of ammonia gas. When the nanocrystalline YbN obtained by the decomposition of $Yb(NH_2)_2$ at 1023 K was used as a sample, YbN immediately took up ammonia upon contact with ammonia, leading to changes from dark brown to reddish brown. For YbN taking up varied amounts of ammonia (NH_3/YbN = 0.11 and 0.25), TPD measurements were made to evaluate the properties of ammonia taken up by YbN (Fig. 3). The NH_3-treated YbN in the NH_3/YbN molar ratio

Table 1
Surface areas of decomposed products as precursors of $Eu(NH_2)_2$, $Yb(NH_2)_2$ and $Yb(NH_2)_3$

Precursor	Evacuation temperature (K)[a]	Phase[b]	Surface area ($m^2\ g^{-1}$)
$Eu(NH_2)_2$	As prepared	$Eu(NH_2)_2$	ca. 0.1
	503	–	111
	573	EuN	107
	773	EuN	49
	1023	EuN	1
$Yb(NH_2)_2$ or $Yb(NH_2)_3$	As prepared	$Yb(NH_2)_2$ ($Yb(NH_2)_3$)	19 (30)[c]
	483	YbNH	73
	573	YbNH	100 (114)[c]
	773	YbN	146 (144)[c]
	1023	YbN	126 (123)[c]

[a] The samples were evacuated at the prescribed temperatures for 1 h.

[b] Evaluated by X-ray diffraction.

[c] The values in parentheses correspond to the surface areas obtained for $Yb(NH_2)_3$.

of 0.11 showed broad desorption peaks of H_2 and N_2 around 800 K; besides, the evolution of both gases occurred approximately at the same time. Upon further NH_3 treatment of YbN to the ratio of 0.25, the desorption of NH_3, other than H_2 and N_2, was additionally observed around 410–420 K. As for the ammonia taken up by NH_3-treated YbN, at least two types of ammonia seem to exist on/in the nanosized YbN; one is molecularly adsorbed ammonia and the other is ammonia undergoing some reaction with YbN. Judging from TPD measurements and the reaction behavior with NH_3, it seems that the first-added ammonia quickly reacts with YbN and that ammonia added in excess is molecularly adsorbed. Since approximately simultaneous desorption of H_2 and N_2 occurred as shown in Fig. 3, the ammonia species taken up exists likely in a molecular form rather than in a decomposed form and decomposed to H_2 and N_2 upon the desorption. The desorption temperatures (700–900 K) of H_2 and N_2 observed here were very similar to the results observed for TPD (Fig. 2) of $Yb(NH_2)_3$. In addition, these temperatures were close to those for the conversion of YbNH into YbN in XRD (Fig. 1). This likely indicates that the NH_3 treatment of nanocrystalline YbN, probably YbN_{1-x}, leads to partial changes to YbNH although the chemical equation is not necessarily satisfied. It is of interest that there was an indication of H_2 uptake by YbN upon contact with hydrogen over 773 K, but not at lower temperatures.

XRD of the NH_3-treated YbN showed diffraction peaks shifted to lower angles. This suggests that the ammonia molecules enter the crystal lattice, resulting in the expansion of crystal constants. When the NH_3-treated sample was heated up to around 973 K under vacuum to desorb the incorporated NH_3, the XRD pattern returned to the one identical with the untreated YbN as shown in Fig. 4. It is recognized elsewhere [3] that such NH_3 uptake by the nanocrystalline YbN and EuN which accompanies changes in crystal structures results in the improvement of catalytic properties.

The uptake of NH_3 by YbN led to a decrease in surface area; YbN showed a drop in surface area from 126 to 73 $m^2\ g^{-1}$ when treated with ammonia in the ratio of 0.28. EuN showed a behavior similar to YbN in NH_3 uptake, but less reactivity than YbN.

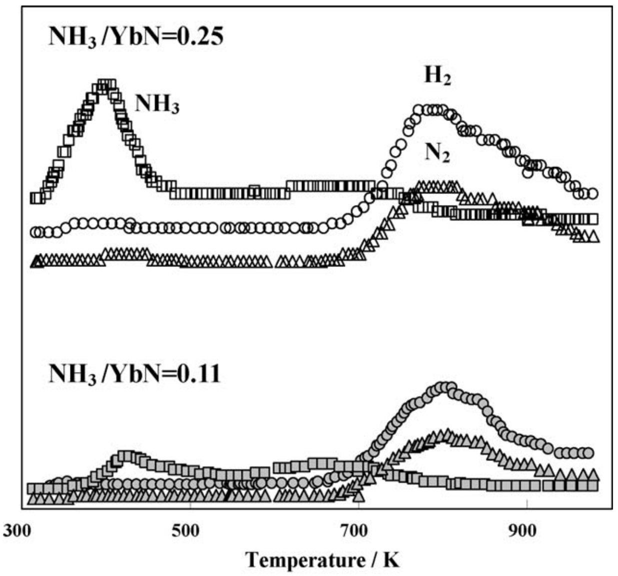

Fig. 3. TPD of NH_3-treated YbN in the NH_3/YbN molar ratios of 0.11 and 0.25.

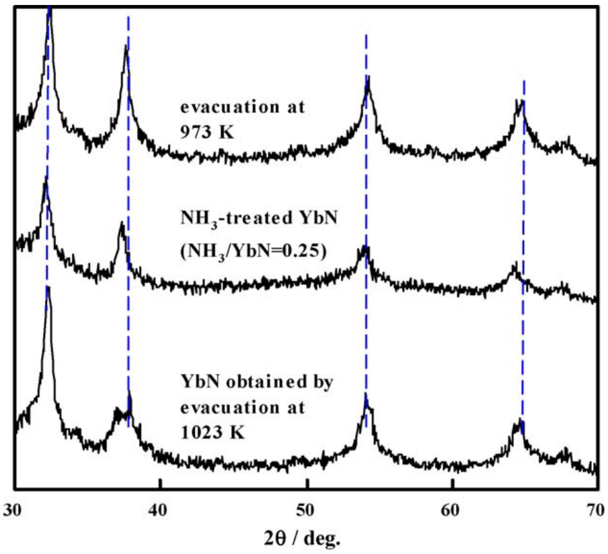

Fig. 4. XRD of YbN, NH_3-treted YbN (NH_3/YbN = 0.25) and NH_3-treated YbN evacuated at 973 K.

References

[1] W.J. Peer, J.J. Lagowski, J. Phys. Chem. 84 (1980) 1110;
J.C. Thompson, Electrons in Liquid Ammonia, Clarendon Press, Oxford, 1976.

[2] H. Imamura, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 29, North-Holland, Amsterdam, 2000, p. 45 (and references therein).

[3] H. Imamura, T. Nuruyu, T. Kawasaki, K. Teranishi, Y. Sakata, Catal. Lett. 96 (2004) 185.

[4] H. Imamura, Y. Sakata, Y. Tsuruwaka, S. Mise, J. Alloys Compd., in press.

[5] F. Hulliger, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, vol. 4, North-Holland, Amsterdam, 2000, p. 160 (and references therein).

[6] K. Howell, L.L. Pytlewski, J. Less-Common Met. 19 (1969) 399.

[7] S. Salot, J.C. Warf, J. Am. Chem. Soc. 90 (1968) 1932.

[8] R. Juza, C. Hadendeldt, Naturwissenschaften 55 (1968) 229.