

Preparation of lutetium nitride by direct nitridation

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Lutetium nitride (LuN), an end member of a new quaternary system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Lu}_2\text{O}_3\text{-LuN}$, was synthesized by direct nitridation of a lutetium metal. The nitridation extent of the lutetium ingot ($10 \times 5 \times 2$ mm) reached about 97% by heating at 1600 °C for 8 h with an applied N_2 pressure of 0.92 MPa; the initial shape of the bulk metal was maintained in the course of nitridation. The resulting nitrated lutetium possessed a moderately low oxygen content (~ 0.7 wt%), which enables the preparation of uncharacterized high nitrogen-containing phases in the Lu-Si-O-N system.

I. INTRODUCTION

In the recent development of rare-earth (RE)-doped silicon nitride (Si_3N_4) ceramics, lutetium oxide (Lu_2O_3) has been found to be a good sintering additive for producing fully dense materials with excellent strength at temperatures up to 1500 °C.¹ The high-temperature properties of Si_3N_4 materials are determined mainly by the grain boundary phase assemblage, and this in turn is determined by the phase relationships in the RE-Si-O-N system. Thus, numerous researches have been devoted to clarifying the phase relationships in the $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-RE}_2\text{O}_3$ (RE = Y,²⁻⁴ La,⁵ Ce,⁶ Yb^{7,8}) pseudoternary systems, and the rare-earth silicon oxynitride phases of $\text{RE}_2\text{Si}_3\text{O}_3\text{N}_4$ (M-phase), RESiO_2N (K-phase), $\text{RE}_4\text{Si}_2\text{O}_7\text{N}_2$ (J-phase), and $\text{RE}_5\text{Si}_3\text{O}_{12}\text{N}$ (H-phase) have been reported. Hirosaki et al.⁹ investigated the phase relationships in the $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Lu}_2\text{O}_3$ system and revealed the presence of a new nitrogen-rich compound, $\text{Lu}_3\text{Si}_5\text{ON}_9$, which coexists with Si_3N_4 and Lu-J-phase¹⁰ at the composition corresponding to the Lu-M-phase. This result indicated the existence of the compatibility triangles across the $\text{Si}_3\text{N}_4\text{-Lu}_2\text{O}_3$ line, triggering the expanding research on the previously unexplored $\text{Si}_3\text{N}_4\text{-Lu}_2\text{O}_3\text{-LuN}$ region of the Lu-Si-O-N quaternary system (Fig. 1).

It is generally acknowledged that the phase relationships of the $\text{Si}_3\text{N}_4\text{-RE}_2\text{O}_3\text{-REN}$ region of the quaternary system are difficult to assess because of the difficulty of

synthesizing a constituent rare-earth nitride in a moderate processing condition; this subject is also rarely found among literature.¹¹⁻¹³ Recently, the phase relationships in the $\text{Si}_3\text{N}_4\text{-YN}$ ¹⁴ and $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-RE}_2\text{O}_3\text{-REN}$ (RE = Y, La)¹⁵ systems were investigated without using the nitride starting material. In both studies, the phase relationships were deduced from samples synthesized mainly by the carbothermal reduction-nitridation of $\text{RE}_2\text{O}_3\text{-SiO}_2$,^{14,15} $\text{RE}_2\text{O}_3\text{-Si}$,¹⁴ or $\text{RE}_2\text{O}_3\text{-Si}_3\text{N}_4$ ¹⁵ mixtures with various RE/Si ratios. It should be noted, however, that this approach is applicable only if the reduction-nitridation of the constituent metal oxide is possible in practice, and precise control of the final composition of the product seems to be rather difficult in this process. Thus, the alternative method (i.e., the solid-state reaction between the three end members) would still be required for other high atomic number rare-earth systems, which allows the above described nitrogen-rich region to be investigated more systematically.

In the work presented here, we report on the synthesis of lutetium nitride by direct nitridation of a bulk Lu metal under a N_2 pressure of <1 MPa. The resulting LuN specimens possessing a sufficiently high nitridation extent are to be used as starting materials for our ongoing study on the phase relationships in the $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Lu}_2\text{O}_3\text{-LuN}$ quaternary system.

II. EXPERIMENTAL

A lutetium ingot was used as a starting material for the synthesis of LuN. The metallic assay was >99.9%, the major non rare-earth impurities being Fe, Mg (<0.01% each) and Ca (<0.05%). The oxygen content was measured to be 0.46 ± 0.04 wt% in the current experiment.

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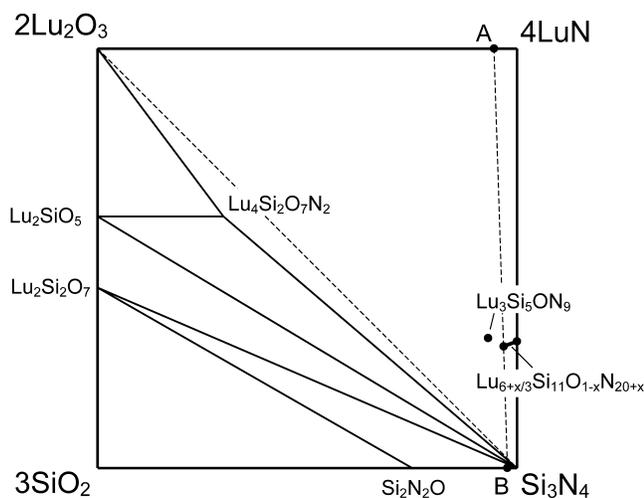
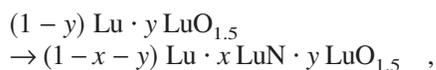


FIG. 1. Phase relationships in the system $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-Lu}_2\text{O}_3\text{-LuN}$ according to our work.⁹ Previously reported new nitrogen-rich phases, $\text{Lu}_3\text{Si}_5\text{ON}_9$ ⁹ and $\text{Lu}_{6+x/3}\text{Si}_{11}\text{O}_{1-x}\text{N}_{20+x}$ ¹⁶ are also indicated. Points A and B indicate the compositions of LuN obtained in this work and of a commercially available Si_3N_4 powder.

Because of the air-sensitivity of the raw material and the nitrided samples, all of the following manipulations were carried out in a pressurized glove box (Unilab, Mbraun GmbH, Garching, Germany) filled with nitrogen, which was continuously purified by passage over an activated copper and molecular sieve. The concentrations of H_2O and O_2 in the box atmosphere were kept normally at a value of <1 ppm. The metal to be nitrided was first cut into pieces of about $10 \times 5 \times 2$ mm and thoroughly polished with #2000 grit SiC paper to remove surface layers. A cleaned and weighed sample was then encapsulated in a double-walled boron nitride crucible and set in a gas-pressure sintering furnace equipped with graphite heating elements (FVPHP-R-10, Fujidempa Kogyo Co., Osaka, Japan). The furnace was evacuated to about 5×10^{-3} Pa before heating to 800 °C, at which a high purity N_2 gas (99.9995%) was introduced into the reactor until the furnace pressure reached the prescribed value. The furnace was subsequently heated to the experimental reaction temperature ($1600\text{--}1700$ °C) at a rate of 10 °C/min, and the temperature was maintained for a soaking time of 2 to 8 h. After cooling to room temperature, the product was transferred to the glove box and reweighed to determine the extent of nitridation from the weight gain. The nitridation extent was calculated taking into account the oxygen impurity in the metal starting material, which was assumed to remain in the samples after nitridation according to the reaction



where x and y denote molar fractions of the nitride and

oxide portions. Thus, the extent of nitridation was defined as $x/(1 - y)$.

X-ray diffraction (XRD) data were collected from a highly nitrided sample using a diffractometer (RINT 2200, Rigaku Co., Tokyo, Japan) operating with $\text{Cu K}\alpha$ radiation at 298 K. The step width was 0.03° and the 2θ range of $18\text{--}155^\circ$ was covered. The sample for XRD analysis was prepared by pulverizing the product to fine powder with an agate mortar and pestle and sealing the powder in a special gas-tight sample holder¹⁷ to prevent oxidation during the measurement. A high-purity Si powder (SRM640b, NIST) was used as an internal standard, and the refined lattice constant was obtained by Cohen's method.¹⁸ Microstructures of the nitrided samples were examined using a field-emission scanning electron microscope (model JSM-6700F, JEOL Co., Tokyo, Japan). Samples for scanning electron microscopy (SEM) analyses were coated with sputtered platinum to reduce the tendency for electrical charge buildup. Bulk density and open porosity were measured by the standard fluid immersion method using *n*-butanol. The selected samples were quantitatively analyzed by the selective hot-gas extraction technique (TC-436, LECO Co., St Joseph, MI, USA) for nitrogen and oxygen. At least four sets of fragmentary samples (~ 30 mg each) were taken from different portions of each bulk product, which were tightly sealed in a tin flux capsule under the box atmosphere prior to analyses.

III. RESULTS AND DISCUSSION

Table I summarizes the results of the nitridation at various temperatures in the range $1600\text{--}1700$ °C for the soaking times of 2–8 h. Nitridation was first conducted at 1600 °C; that is, well below the melting point of Lu (ca. 1660 °C) with a soaking time of 2 h and an applied N_2 pressure of 0.10 MPa (sample A). The nitridation extent of the sample thus obtained was as low as 75%, and the fractured surface exposed a visible unreacted metallic core. A marked increase in conversion was attained by increasing the N_2 pressure to 0.92 MPa, and a sample with a nitridation extent of 85% was obtained (sample

TABLE I. Direct nitridation of bulk lutetium under various reaction conditions.

Sample	Reaction temperature (°C)	Holding time (h)	Applied N_2 pressure (MPa)	Nitridation extent ^a (%)
A	1600	2.0	0.10	74.5
B	1600	2.0	0.92	85.0
C	1600	4.0	0.92	88.8
D	1650	2.0	0.92	93.6
E	1700	2.0	0.92	94.3
F	1600	8.0	0.92	96.0
G	1650	8.0	0.92	95.9

^aDetermined by the weight gain measurements.

B). Longer soaking (4 h) raised the conversion considerably to 89% (sample C), and the resulting product exhibited uniform fracture cross-sections, indicative of a high degree of nitridation. Increasing the processing temperature also enhanced the nitridation (sample D), whereas heating above the melting point of Lu resulted in only a slight increase of the nitridation extent (sample E). Duration of heating was effective for further nitridation, and samples possessing nitridation extents as high as approximately 96% were finally obtained with a soaking time of 8 h, regardless of the processing temperatures of 1600 or 1650 °C (samples F and G).

The starting metals turned grayish black by experiencing nitridation, while the initial shape of the bulk samples were kept essentially intact in all runs made. Thus, the products were obtained in a consolidated form, which could easily be pulverized in an agate mortar. The black coloration of the nitride changed to a dark brown on exposure to ambient air in several days, and further exposure resulted in the disconsolidation of the bulk product and conversion to a white amorphous powder with an oxygen content of 16.2 wt%, which is in between the values of Lu_2O_3 (12.1 wt%) and $\text{Lu}(\text{OH})_3$ (21.2 wt%). This undue oxidation/hydrolysis was almost completely suppressed by keeping the samples in the purified N_2 atmosphere of the glove box, and the increase of the oxygen content was found to be negligibly small (<0.05 wt%), even after 1 year.

XRD analysis was performed on the sample synthesized at 1600 °C with a soaking time of 8 h (sample F). The spectrum revealed the characteristic pattern of rare-earth monopnictides in NaCl-type structure, though the reflections were relatively broad and severely blurred at higher angles, making a precise determination of the peak positions difficult. To improve crystallinity of the product, a two-stage heating with additional high-temperature annealing at 1900 °C for 2 h was conducted (sample F2). The sample thus obtained exhibited a diffraction spectrum of LuN consisting of peaks whose line shapes are essentially single, with a trace of crystalline Lu_2O_3 . The refined lattice constant was calculated to be $a = 4.7563(4)$ Å, which is in close agreement with that reported by Didchenko and Gortsema ($a \sim 4.759$ Å).¹⁹ The indexed powder pattern for the total of 13 diffraction lines observed in the 2θ range up to 155° is given in Table II.

Figure 2 shows the typical microstructure of the products synthesized at temperatures from 1600 to 1700 °C. The nitrided samples exhibited rather porous microstructures consisting of isolated grains of around 1–3 μm. No significant difference in microstructure formation was observed throughout the temperature range investigated in the current study. To evaluate the microstructures quantitatively, the bulk density and open porosity were measured for the three samples having high nitridation

TABLE II. X-ray powder diffraction data for synthesized LuN.

h	k	l	$2\theta_{\text{obs}}/\text{deg.}$	$d_{\text{obs}}/\text{Å}$	$(I/I_0)_{\text{obs}}$
1	1	1	32.569	2.7470	100
2	0	0	37.787	2.3788	76
2	2	0	54.520	1.6817	35
3	1	1	64.960	1.4344	27
2	2	2	68.231	1.3734	9
4	0	0	80.711	1.1896	4
3	3	1	89.799	1.0913	8
4	2	0	92.771	1.0639	9
4	2	2	104.980	0.9710	6
5	1	1	114.669	0.9150	5
4	4	0	132.796	0.8406	2
5	3	1	146.690	0.8040	5
4	4	2	152.544	0.7929	3

$$a = 4.7563(4) \text{ Å.}$$

$$F_{13} = 28 (0.036, 13).$$

extents of >90%, and the resulting data are summarized in Table III. As indicated by the SEM analyses, the values of bulk density were not very different among the three samples, ranging from 9.48 to 9.55 g·cm⁻³, the corresponding relative density being 82.0–82.8%. Their values of open porosity were found to be almost equal to the total pore volume of each sample, meaning that open channels were formed through the bulk surface to the core of the sample during the course of nitridation. This microstructural evolution can be attributed to the fact that the conversion of Lu with the h.c.p. structure to LuN involves a considerable reduction of the molar volume ($V_{\text{LuN}}/V_{\text{Lu}} = 0.90$), which may lead to the formation of a nonprotective, porous nitride layer on the bulk surface, allowing N_2 penetration into the core of the sample and continuous inward growth of the product. This seems to be the main reason why almost complete nitridation of the millimeter-sized bulk materials could be achieved in this reaction system, and contrasts with other common systems such as Al ($V_{\text{AlN}}/V_{\text{Al}} = 1.26$) and Si ($V_{\text{Si}_3\text{N}_4}/3V_{\text{Si}} = 1.22$), in which the reactions are restricted to the formation of a thin protective layer on the surface.^{20,21} These results also suggest the promising applicability of this direct nitridation process to other high atomic number rare-earth systems such as Ho, Er, and Tm.

The nitrogen and oxygen analyses were conducted by the selective hot-gas extraction method for two different batches of samples that exhibited the highest conversion of all (samples F and G). The analytical results of the nominal composition expressed as $(1 - x - y) \text{ Lu} \cdot x \text{ LuN} \cdot y \text{ LuO}_{1.5}$ are summarized in Table IV. The sum of the nitride and oxide portion ($x + y$) was found to be lower than unity in both cases, indicating that 2.1–2.7% of metals remained in the as-synthesized samples. The corresponding nitridation extents are calculated to be 97.8% for sample F and 97.1% for sample G, consistent with values estimated from the weight gain measurements (Table I) when taking into account probable

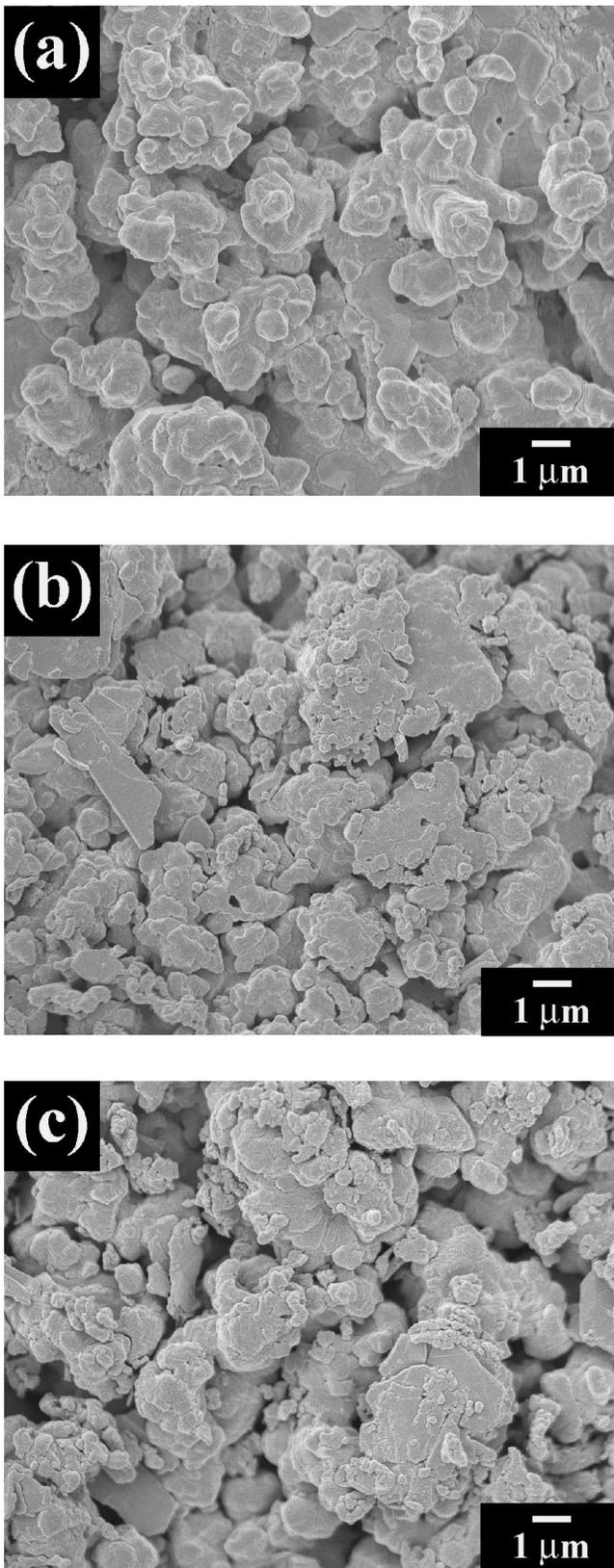


FIG. 2. Field-emission scanning electron microscopy photographs of as-prepared bulk surfaces of the samples synthesized at (a) 1600 °C, (b) 1650 °C, and (c) 1700 °C with a soaking time of 2 h.

TABLE III. Measured bulk density and open porosity values for nitrated samples.

Sample	Bulk density ($\text{g} \cdot \text{cm}^{-3}$)	Open porosity (%)	Relative density (%)
F	9.53 ± 0.01	16.4 ± 0.1	82.2
D	9.55 ± 0.01	17.0 ± 0.2	82.8
E	9.48 ± 0.01	17.2 ± 0.1	82.0

weight loss by evaporation during the heat treatment. The nitridation in excess of unity was detected for annealed sample F2, and the amount of excess is no longer within the estimated analytical error of ± 0.003 . This observation may indicate the possible oxygen dissolution and consequent cation deficiency in LuN, which will be discussed in our forthcoming studies. The oxygen content of the as-synthesized samples was around 0.7 wt%, which is low enough for the preparation of the monophasic samples of $\text{Lu}_3\text{Si}_5\text{ON}_9$ and $\text{Lu}_6\text{Si}_{11}\text{ON}_{20}$ ¹⁶ (Fig. 1). Sample F2 exhibited an appreciably higher oxygen content, indicating that a high-temperature heat treatment is not effective in reducing oxygen impurities despite the use of a graphite-lined furnace. We have now obtained several nitrogen-rich samples in the Si_3N_4 – Lu_2O_3 –LuN region by the solid-state reaction at 1850 °C using the nitride synthesized, and detailed analyses of the phase relationships are currently in progress.

IV. CONCLUSION

The synthesis of LuN was performed by direct nitridation of bulk Lu metal under practical processing conditions, to establish an approach to investigating the phase relationships in the Si_3N_4 – SiO_2 – Lu_2O_3 –LuN system. Highly nitrated samples (85–97%) were successfully prepared at processing temperatures of 1600–1700 °C within 8 h, under a N_2 pressure of 0.92 MPa. The nitrated samples were obtained in a consolidated form having an open porosity of approximately 17%, which consisted of micrometer-sized grains and could easily be pulverized into a fine powder. The porous microstructure formation could be attributed to the molar volume reduction resulting from the conversion of h.c.p. metal to the nitride in a NaCl-type structure, which allowed N_2 penetration into

TABLE IV. Analytical results of the nominal composition of nitrated samples: $(1 - x - y) \text{Lu} \cdot x\text{LuN} \cdot y \text{LuO}_{1.5}$.

Sample	Nitrogen content ^a (wt%)	Oxygen content (wt%)	x	y	Nitridation extent ^b
Raw material		0.46 ± 0.04		0.034	
F	6.84 ± 0.03	0.70 ± 0.01	0.924	0.055	0.978
G	6.75 ± 0.03	0.77 ± 0.02	0.912	0.061	0.971
F2	6.91 ± 0.02	0.93 ± 0.02	0.937	0.074	1.012

^a7.41 wt% for ideal LuN composition.

^bDefined as $x/(1 - y)$.

the core of the ingots and thus promoted full nitridation of the bulk samples. The nitrided lutetium obtained possessed a sufficiently low oxygen content (~ 0.7 wt%), which permits the synthesis of novel high nitrogen-containing phases (e.g., $\text{Lu}_3\text{Si}_5\text{ON}_9$ and $\text{Lu}_6\text{Si}_{11}\text{ON}_{20}$).

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