論文 High Temperature Decarbonization of Neodymium Sesquisulfide by Hydrogen, Hydrogen Sulfide and Ammonia*

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The removal of carbon impurity from Nd₂S₃ has been studied by heating in the gases of 4 % H₂/N₂, H₂S and NH₃. When the sulfide containing 1,200 mass ppm carbon impurity was heated in 4 % H₂/N₂ or H₂S at 1,600 °C for 1 h, the carbon content decreased to 600 mass ppm. With NH₃ gas, the carbon content decreased to 850 mass ppm by heating at a lower temperature of 1,000 °C for 1 h. Prolonged heating for 5 h resulted in further decrease of carbon content to 600 ppm. The mechanism of reaction of carbon with the above different gases is discussed in relation to the free energy change associated with the reactions. The phase transformation from α - to γ -Nd₂S₃ was observed after the decarbonization with 4 % H₂/N₂ and H₂S, while it did not occur during the low temperature processing at 1,000 °C in NH₃.

KEY WORDS : Neodymium, Sulfide, Decarbonization, Hydrogen, Hydrogen Sulfide, Ammonia

1. Introduction

Bonding in sulfides is generally more covalent than that in corresponding oxides. In some cases, the covalent bonding in sulfides gives rise to interesting properties which have technological applications. Rare-earth sesquisulfides are the constituents of mixed sulfides, i.e. palladium sulfide bronzes¹⁾, rock-salt type ALnS₂ compounds²⁾ and other intersulfide compounds.

Several methods have been adopted for the preparation of the rare-earth sulfides^{3)–5)}. The one most widely used among them in laboratory is direct reaction of rare-earth metal with sulfur⁶⁾. However, pure metals are expensive and they are easily oxidized during handling in air. Sulfurization of oxides with hydrogen sulfide is another method for preparing rare-earth sulfides since high purity oxides with high metallic purities are easily available⁷⁾. Rare-earth sulfides can also be obtained by the reaction of oxysulfide with hydrogen sulfide in the presence of carbon⁸⁾ at high temperature. However, at very high temperatures there is a change in stoichiometry of the sulfide or decomposition⁹⁾ may occur.

As an alternative method to prepare the rare-earth sulfides, the reaction of sulfates with carbon in the presence of sulfur has been reported¹⁰⁾. Nevertheless, the sulfides ob-

tained by this method often contain a fairly large amount of carbon. In our recent studies, an improved method using carbon disulfide, CS₂, has been exploited^{11)–13)}. Although CS₂ is a powerful sulfurizing agent for oxides or sulfates, the sulfides produced using CS₂ often contain a significant amount of carbon.

This paper describes the decarbonization of Nd₂S₃ synthesized by the reaction of Nd₂(SO₄)₃ with CS₂. The impurity carbon was made to react with either H₂, H₂S or NH₃ gas at high temperatures. The effect of heating temperature and time on carbon removal was studied for the three gases.

2. Experimental

2 · 1 Materials

Analytical grade CS₂ with a boiling point of 46~47 °C and maximum water content of 0.02 % was obtained from Wako Pure Chemicals Co., Ltd. and used as received. Anhydrous neodymium sulfate, Nd₂(SO₄)₃, was obtained by heating neodymium sulfate octahydrate, Nd₂(SO₄)₃ · 8 H₂O, (99.9 %, purchased from Nippon Yttrium Co., Ltd.) at 450 °C in a vacuum of 10 Pa for 1 h. Nitrogen gas of 99.99 % purity, 4 % H₂/N₂ gas mixture, H₂S gas of 99.99 % purity and NH₃ gas of 99.999 % purity (CH₄ < 1 ppm) were obtained from Nippon Sanso Co., Ltd. and used as received.

2 · 2 Preparation of neodymium sesquisulfide

Neodymium sesquisulfide, Nd₂S₃, was prepared by heating anhydrous Nd₂(SO₄)₃ in a stream of CS₂/N₂ at 900 °C for 4 h. The gas mixture of CS₂ and N₂ was obtained by bubbling N₂ gas through the liquid CS₂ at a flow rate of 100 ml/min. The sulfide produced was reddish brown, and it was identified as α -Nd₂S₃ (orthorhombic)¹⁴⁾ by powder X-ray diffrac-

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1: Gas cylinder (N_2 , 4% H_2/N_2) 2: Gas cylinder (H_2S , NH_3) 3: Gas flowmeter 4: Valve 5: Gas mixer 6: Halogen lamp furnace 7: Quartz tube 8: Sample 9: Thermocouple 10: Bubbler 11: Absorbent

Fig. 1 Schematic drawing of the experimental apparatus.

tion analysis. The other phases such as NdS (cubic)¹⁵⁾, $\gamma-Nd_2S_3$ (cubic, Nd_3S_4)¹⁶⁾, NdS_2 (tetragonal)¹⁷⁾, Nd_2O_2S (trigonal)¹⁸⁾ and $Nd_2O_2SO_4$ (orthorhombic)¹⁹⁾ were not observed. The lattice parameters of $\alpha-Nd_2S_3$ calculated using the LCR 2 program²⁰⁾ are $a = 7.440 \pm 0.001$, $b = 15.514 \pm 0.002$ and $c = 4.027 \pm 0.001$ Å. They compare well with the reference values of $a = 7.442$, $b = 15.519$ and $c = 4.029$ Å¹⁴⁾. The sulfur content of Nd_2S_3 obtained by chemical analysis was 24.01 wt % which corresponds to the chemical formula $Nd_2S_{2.84}$. The obtained Nd_2S_3 contained $1,160 \pm 110$ mass ppm of carbon as an impurity.

2 · 3 Experimental procedure

Fig. 1 shows a schematic drawing of the reaction system used. The neodymium sesquisulfide obtained by synthesis was finely powdered in an agate mortar followed by pressing into a pellet of 10 mm in diameter. The pellet was placed on an alumina supporting tube at the center part of a halogen lamp furnace (Shinku-Riko, PRC MR-H500). Before heating the sample, the reaction system was evacuated by a rotary pump and refilled with N_2 at the ambient pressure. Then, the 4% H_2/N_2 gas mixture, H_2S or NH_3 gas was flowed through the tube at a rate of 60 ml/min.

The furnace temperature was raised at a constant rate of 100 °C/min up to a set temperature using a programmable controller (OMRON Type ES100P). After the reaction at a fixed temperature, the power supply to the furnace was cut off and the sample was kept in the flowing gas until it cooled to room temperature. The temperature of the sample was measured by the Pt/Pt-13% Rh thermocouple which was attached to the top end of the supporting tube.

After the reaction, the pellet was ground in an agate mortar for X-ray diffraction and chemical analyses.

2 · 4 Powder X-ray diffraction analysis

The X-ray powder diffraction analysis was carried out with a Rigaku Type RAD-IC diffractometer using $CuK\alpha$ radiation (40 kV, 20 mA) monochromatized with curved pyrolytic graphite. Intensity and least-squares lattice parameter calculations were carried out with the programs LAZY-PULVERIX²¹⁾ and LCR2²⁰⁾, respectively.

Fig. 2 Change of carbon content of $\alpha-Nd_2S_3$ as a function of temperature. The sulfide was heated in a stream of 4% H_2/N_2 , H_2S or NH_3 gas for 1 h at each temperature.

2 · 5 Chemical analysis

The sulfur content of neodymium sulfide was determined by the EDTA titration after the oxidation of S^{2-} ion and S^0 to SO_4^{2-} using bromine oxidizer²²⁾.

Carbon was determined by oxygen gas fusion (induction heating type)-infrared absorptiometry using a Horiba Type EMGA-520 analyzer. The standard samples of steel supplied by the LECO Corp. (No. 501-672 and 501-674) and Steel Institute of Japan (No. JSS 201-11) were used for the preparation of calibration curve for carbon. Carbon contents were obtained as the average of three determinations of powdered samples.

Nitrogen in neodymium sulfide was determined by inert gas fusion-infrared absorptiometry using Horiba Type EMGA-2200 analyzer.

3. Results and Discussion

3 · 1 Effect of heating temperature

A sample of $\alpha-Nd_2S_3$ was heated in the 4% H_2/N_2 gas mixture for 1 h at temperatures from 1,200 to 1,600 °C. The change

of carbon content is shown in Fig. 2 (circle marks) as a function of heating temperature. The color of the sulfide did not change when heated at 1,200 °C, but it changed to light green at 1,400 °C and to light blue at 1,600 °C. Since the colors of α - and γ -Nd₂S₃ are reddish brown and pale blue, respectively, the color change in the samples suggests the formation of γ -Nd₂S₃ at higher temperatures. The carbon content of the starting material is also given in the figure as a double circle. The carbon content of the sulfides shows a monotonic decrease with increasing heating temperature. The carbon content of the sample heated at 1,600 °C is 600 mass ppm, which is half of the carbon content in the initial Nd₂S₃. The stoichiometry and the molecular weight of neodymium sesquisulfide was found to change slightly during the high temperature exposure because of preferential evaporation of sulfur from the sample. This effect is, however, of the order of several tens of mass ppm in the calculation of carbon content in Nd₂S₃.

Next, the reddish brown α -Nd₂S₃ pellet was heated in a flow of H₂S for 1 h at temperatures of 1,200, 1,400 and 1,600 °C. The change of carbon content in the above products is shown in Fig. 2 (triangle marks). The amount of carbon in the products gradually decreased with increasing temperature from 1,200 to 1,600 °C. The removal of carbon seems to be effective at 1,600 °C. The result is close to that obtained with 4 % H₂/N₂ mentioned above.

The effect of temperature on the decarbonization of α -Nd₂S₃ with NH₃ (reaction time 1 h) is indicated in Fig. 2 (diamond marks). Below 900 °C, no significant change of the carbon content was observed. However, the carbon content rapidly decreased at 1,000 °C; at higher temperatures the rate of the decrease was rather small.

3 · 2 Effect of heating time

The change of carbon content of α -Nd₂S₃ as a function of heating time is shown in Fig. 3. When α -Nd₂S₃ was heated in 4 % H₂/N₂ gas mixture at 1,600 °C (circle marks), the decarbonization of α -Nd₂S₃ proceeded rapidly in the first 10 min, and the curve leveled off over the next 30 min. This flat-

Fig. 3 Change of carbon content of α -Nd₂S₃ as a function of heating time. The sulfide was heated in a stream of 4 % H₂/N₂ (1,600, 1,700 °C) or H₂S (1,600 °C).

Fig. 4 Change of carbon content of α -Nd₂S₃ as a function of heating time. The sulfide was heated in a stream of NH₃ gas at 900, 1,000 and 1,200 °C.

tening may be ascribed to the obstruction of evolution of vapor species such as CS₂ and H₂S as a result of the sintering of pellet at high temperature. If the sample was heated at 1700 °C the rate of decarbonization in the first 10 min (triangle mark) was higher and the carbon content decreased to 700 mass ppm during this period.

In the case of the reaction with H₂S (square marks), almost the same results were obtained as those with 4 % H₂/N₂ gas mixture. This fact suggests that the reaction schemes for carbon removed from α -Nd₂S₃ are closely related for the two different gases of H₂S and 4 % H₂/N₂.

For the reaction of α -Nd₂S₃ with NH₃, the effect of heating time was studied at 900, 1,000 and 1,200 °C. The results are shown in Fig. 4. At 900 °C, the carbon content rather gradually reduced with increasing heating time. The carbon content was still 900 mass ppm in the sample heated for 5 h. However at 1,000 °C, the carbon content decreased more rapidly and reached a value near 600 mass ppm after 5 h. This carbon content is comparable with that obtained by the reaction with 4 % H₂/N₂ or H₂S at 1,600 °C for 1 h. The decrease of

Fig. 5 Change of standard Gibbs energy for some related reactions as a function of temperature (C(s): graphite).

the carbon content at 1,200 °C was nearly the same as that at 1,000 °C. Thus the process using NH_3 has the advantage of decreasing the carbon content at a relatively low temperature of 1,000 °C, although the process takes several hours.

3 · 3 Thermodynamic evaluation of the purification process

Fig. 5 shows the standard Gibbs energy change (ΔG°) for the reaction listed below, calculated by using the data from MALT 2²³⁾.

It is seen from the figure that the ΔG° values for eq. (1) are significantly positive at the temperatures of the present experiment suggesting that the removal of carbon from Nd_2S_3 by H_2 as CH_4 is not favorable at high temperatures: The partial pressure of CH_4 in equilibrium with carbon and H_2 (1 atm) are calculated to be 3.00×10^{-3} and 5.95×10^{-4} atm at 1,200 and 1,600 °C, respectively. The pressure is low at 1,200 °C and it still more lowers at 1,600 °C. However, the amount of carbon impurity was significantly reduced by heating at high temperatures of 1,600 and 1,700 °C. Therefore, the removal of carbon from $\alpha\text{-Nd}_2\text{S}_3$ is considered to have proceeded through a different reaction. In the case of reaction (2) to form C_2H_2 from carbon and H_2 , ΔG° decreases with increasing temperature giving lower ΔG° than reaction (1) at 1,700 °C. But the ΔG° values of eq. (2) around this temperature are not low enough to proceed the reaction significantly (Fig. 5). The reaction, which seems to be more possible, may occur between carbon and sulfur in the solid sample to form $\text{CS}_2(\text{g})$ in the reducing atmosphere of 4 % H_2/N_2 gas mixture:

The above reaction consists of the sum of the decomposition reaction $6\text{Nd}_2\text{S}_3(\text{s}) = 4\text{Nd}_3\text{S}_4(\text{s}) + \text{S}_2(\text{g})$ and eq. (3). From the negative ΔG° values for eq. (3) shown in Fig. 5, the formation of $\text{CS}_2(\text{g})$ appears to be feasible at high temperatures, because the partial pressure of S_2 over Nd_2S_3 sample is considered to be fairly high. The decrease of the sulfur amount in the neodymium sesquisulfide treated in 4 % H_2/N_2 as stated in Sec. 3 · 1 is in line with eq. (6).

For the reaction between carbon and H_2S (eq. (4)), the change of ΔG° is shown in Fig. 5 as line 4. The ΔG° values are negative above 1,334 °C, which explains the rapid decrease of the carbon content in Nd_2S_3 at high temperature (Fig. 2). In this case, the amount of sulfur in the sample was found to increase with increasing heating temperature: the x-values of NdS_x obtained at 1,200, 1,400 and 1,600 °C were 1.28, 1.35 and 1.39, respectively. From the calculation of the partial pressures of H_2 , S_2 and H_2S in equilibrium (eq. (5)) for the total pressure of 1 atm by using MALT 2²³⁾, the partial pressure of S_2 are low at 800 °C ($p(\text{S}_2) = 0.03$ atm). But the pressure becomes significantly high over 1,000 °C, e.g. $p(\text{S}_2) = 0.25$ atm at 1,600 °C. The higher content of sulfur in Nd_2S_3 than that heated in H_2 atmosphere is therefore, considered to be caused

by the high S_2 partial pressure in H_2S .

When NH_3 gas was used, the removal of carbon proceeded effectively at relatively low temperatures of 1,000 and 1,200 °C as mentioned in Sec. 2. 1. At these temperatures, NH_3 nearly quantitatively decomposed according to the reaction:

If there is no trace of NH_3 in the gaseous phase, the reaction behavior would be the same as that with 4 % H_2/N_2 gas mixture. Actually, the carbon content was much smaller after the reaction in NH_3 at 1,200 °C (Fig. 2). This lowering in the carbon content is assumed to be caused by the high reactivity of hydrogen freshly formed by decomposition. According to Serizawa et al.²⁴⁾, such hydrogen is in a monoatomic state and is so reactive that the carbon in the sulfide is removed by forming volatile hydrocarbons.

It is useful to consider the possibility of formation the neodymium nitride and/or hydride in NH_3 gas at high temperature. Since the thermodynamic data for NdN are not available, we consider the free energy change for the following reaction instead:

The ΔG° values of the above reaction are highly positive, i. e. +586.2 and +362.3 kJ/mol at 25 and 1,500 °C, respectively: The formation of nitride, NdN , is not feasible thermodynamically. The nitrogen content in the products obtained by the reaction of Nd_2S_3 with 4 % H_2/N_2 gas mixture was less than the detection limit of the analyzer. For the following reaction to form hydride:

ΔG° is again highly positive; +897.6 kJ/mol at 927 °C. The above reaction cannot be proceed. Also, NdH_2 is unstable above 900 °C decomposing into Nd metal and H_2 ²⁵⁾.

3 · 4 Phase transformation

Fig. 6 X-ray diffraction patterns of the products obtained by heating $\alpha\text{-Nd}_2\text{S}_3$ in 4 % H_2/N_2 gas mixture for 1 h at temperatures 1,200, 1,400 and 1,600 °C.

Fig. 7 X-ray diffraction patterns of the products obtained by heating α -Nd₂S₃ in NH₃ gas for 1 h at 1,000 and 1,200 °C.

After α -Nd₂S₃ was heated in 4 %H₂/N₂ gas mixture at 1,200, 1,400 and 1,600 °C for 1 h, the powder X-ray diffraction patterns were taken. The results are shown in Fig. 6 together with the calculated patterns for α - and γ -Nd₂S₃ by LAZYPULVERIX²¹⁾ using the reported data^{14) 16)}. Both α - and γ -Nd₂S₃ phases were identified in all the products obtained. The intensities of the peaks for γ -Nd₂S₃ phase increased when the reaction temperature was raised from 1,200 to 1,600 °C.

The sulfur contents of the products determined by the EDTA titration are $x = 1.26, 1.35$ and 1.31 of NdS_x for 1,200, 1,400 and 1,600 °C, respectively. These contents are smaller than that of the original Nd₂S₃. This sulfur deficiency may be caused by the formation of γ -phase neodymium sesquisulfide having the atome ratio S/Nd = 1.33.

For the reaction in H₂S gas for 1 h at temperatures of 1,200, 1,400 and 1,600 °C, the powder X-ray diffraction patterns for the products were almost the same as those for the samples heated in 4 %H₂/N₂ gas. The peak intensities of γ -Nd₂S₃ increased with increasing heating temperature. At 1,600 °C, the γ -Nd₂S₃ phase was dominant and the peaks of α -Nd₂S₃ phase observed were small. The sulfur contents of the products were $x = 1.28, 1.35$ and 1.39 of NdS_x for 1,200, 1,400 and 1,600 °C, respectively. These values are slightly higher than those of 4 %H₂/N₂ products reflecting the higher sulfur partial pressure in H₂S (0.25 atm at 1,600 °C).

The powder diffraction patterns of the α -Nd₂S₃ sample reacted with NH₃ at 1,000 and 1,200 °C are shown in Fig. 7. The pattern for starting material α -Nd₂S₃ is also given in Fig. 7 for comparison. No significant difference was observed in the two diffraction patterns of the starting material and the sample processed at 1,000 °C. The transformation from α - to γ -Nd₂S₃ did not occur by heating at 1,000 °C. However, several peaks of γ -Nd₂S₃ (asterisk marks) appeared in the pattern of the sample heated at 1,200 °C. The γ -Nd₂S₃ phase increased with increasing heating temperature above 1,200 °C. These results, which are the same as those for the samples heated in 4 %H₂/N₂ gas mixture at comparable temperature, suggest that the transformation from α - to γ -Nd₂S₃ phase takes place

between 1,000 and 1,200 °C. These data are consistent with the observation of Besançon on that the transformation occurred at 1,180 °C²⁶⁾.

4. Conclusions

When the sulfide containing 1,200 mass ppm carbon impurity was heated in 4 %H₂/N₂ or H₂S at 1,600 °C, the carbon content decreased to 600 mass ppm in 1 h. In 4 %H₂/N₂ atmosphere, thermodynamic calculation suggests that the carbon impurity in Nd₂S₃ is removed as CS₂ by the reaction with sulfur in Nd₂S₃, while in H₂S streams it is removed as CS₂ by the reaction with decomposed sulfur from H₂S. With NH₃ gas, the carbon content decreased to 850 mass ppm by heating at a lower temperature of 1,000 °C for 1 h. Prolonged heating for 5 h resulted in further removal of carbon to 600 ppm. In this case the freshly formed hydrogen by the decomposition of NH₃ is so reactive that the carbon in the sulfide is considered to be removed by forming volatile hydrocarbons. The reaction in NH₃ is easily applicable because of lower heating temperature. The phase transformation from α - to γ -Nd₂S₃ was observed after the decarbonization with 4 %H₂/N₂ and H₂S accompanied by the sulfur deficiency in the sulfides, while the phase transformation did not occur during the low temperature processing at 1,000 °C in NH₃.

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水素、硫化水素およびアンモニアによるネオジムセスキ硫化物の高温脱炭

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水素、硫化水素あるいはアンモニア雰囲気における加熱処理による金属硫化物中の不純物炭素の除去について調べた。不純物炭素を1,200 mass ppm 含有する Nd₂S₃ を4%水素/窒素あるいは硫化水素雰囲気中、1,600℃において1時間加熱すると、炭素含有量は600 mass ppm まで減少した。アンモニアを用いた場合、1,000℃という低温において1時間加熱すると炭素含有量は850 mass ppm まで減少した。5時間加熱した場合には炭素量を600

mass ppm まで低下させて高純度化することができた。これらの反応ガスと炭素との反応機構について反応の自由エネルギー変化を用いて検討した。

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 キーワード：ネオジム、硫化物、脱炭、水素、硫化水素、アンモニア