ELSEVIER

Thermochimica Acta 244 (1994) 117–129

thermochimica acta

Thermogravimetric study of carbon reduction of $Nd_2(SO_4)_3$

Milan Skrobian [1], Nobuaki Sato *, Masatoshi Saito, Takeo Fujino

Institute for Advanced Materials Processing, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-77, Japan

Received 29 December 1993; accepted 14 March 1994

Abstract

The possibility of sulfide synthesis by carbon reduction of neodymium sulfate was studied by the thermogravimetric technique. Anhydrous $Nd_2(SO_4)_3$ was formed by heating $Nd_2(SO_4)_3 \cdot 8H_2O$ in vacuum or in air at 300°C. When $Nd_2(SO_4)_3$ was mixed with annealed carbon and heated in nitrogen, neodymium oxysulfide Nd_2O_2S was formed at 880°C. However, when $Nd_2(SO_4)_3$ was mixed with activated carbon, the products after heating at the same temperature comprised a mixture of neodymium sulfide Nd_3S_4 with Nd_2O_2S. The ratio of Nd_3S_4 to Nd_2O_2S was found to vary with the reaction conditions.

Keywords: Activated carbon; Carbon; Neodymium oxysulphide; Neodymium sulphate; Neodymium sulphide; TG

---

1. Introduction

It is known that the sulfides or oxysulfides of the rare-earth elements (RE) can be prepared by various methods. Direct reaction of RE metal with sulfur vapor yields RE sulfides with well defined chemical compositions. However, RE metals are not only very sensitive to air oxidation but also expensive. If sulfides can be prepared from RE compounds rather than the RE metals themselves, such a method of

---

* Corresponding author.

[1] On leave from the Department of Non-Ferrous Metallurgy, Technical University, Letna 9, 043 85 Kosice, Slovakia.

SSDI 0040-6031(94)01802-N

synthesis would have the potential for wide application. For synthesizing the sulfides, H_2S or CS_2 is used as a reducing agent as well as the source of sulfur [1,2]. According to Eastman et al. [3], H_2S does not give Ce_2S_3 in the reaction with CeO_2 at temperatures between 1200 and 1400°C. Also, Sc_2S_3 has not been prepared in a pure form free from Sc_2O_2S below 1450°C [4]. These results suggest that high temperatures are required for the reduction of oxides by H_2S. If, instead, carbon is used as a reducing agent with the RE sulfates, their sulfides should be formed provided that only oxygen is removed, leaving the sulfur of the sulfates in the crystal. However, no reports of the synthesis of sulfides by carbon reduction appear to have been published.

This work is concerned with the reaction of neodymium sulfate with carbon under the condition of increasing temperature. In order to determine the decomposition and/or reduction of the neodymium sulfate as a function of temperature and reaction time, thermogravimetric measurements were carried out.

2. Experimental

2.1. Materials

Anhydrous neodymium sulfate $Nd_2(SO_4)_3$ was prepared by heating $Nd_2(SO_4)_3 \cdot 8H_2O$ at 450°C in a vacuum of ≈ 10 Pa for 1 h. The octahydrate with purity $> 99.9\%$ was obtained from Nippon Yttrium Co., Ltd.

Activated carbon with the specification 10% (maximum) weight loss on drying at 105°C and 2% (maximum) residue after ignition was obtained from Wako Pure Chemicals Co., Ltd. Annealed carbon was obtained by heating the activated carbon in a stream of N_2 at 1100°C for 1 h.

2.2. Thermogravimetric procedure

The calculated amounts of $Nd_2(SO_4)_3$ and carbon were intimately mixed in an agate mortar. A quartz crucible containing the weighed mixture was suspended from a quartz spring at a position 5 mm below the center of the uniform temperature zone (± 1°C). The temperature of the specimen was measured with a Pt/Pt + 13% Rh thermocouple placed at the center of the uniform temperature zone in contact with the outer wall of the reaction tube. In some experiments, the reaction tube was evacuated to remove moisture from the carbon. Before heating, the reaction tube was refilled with N_2 up to ambient pressure.

The furnace temperature was raised at constant rate using a programmable controller. The fluctuation of the temperature at holding mode was within ± 1°C at 1000°C. The sensitivity of the quartz spring was 12.76 mg mm^{-2}. The position of the sharp edge of the quartz wire below the spring was optically read with a high precision levelmeter to ≈ 0.03 mm, which corresponded to a weight sensitivity of ≈ 0.4 mg. The weight of the samples before and after the reaction was checked with a laboratory-type electronic balance to ± 0.1 mg.

2.3. X-ray diffraction analysis

X-ray powder diffractometry was carried out using a Rigaku Type RAD-IC diffractometer with Ni filtered Cu Kα radiation (40 kV, 20 mA). The slit system was 1°–0.15 mm–1°. Intensity calculation of the diffraction lines was performed using the LAZY PULVERIX program [5].

3. Results and discussion

3.1. Decomposition of $Nd_2(SO_4)_3 \cdot 8H_2O$

The results of thermogravimetric studies on $Nd_2(SO_4)_3 \cdot 8H_2O$ are shown in Fig. 1. Curve 1 (open circles) in the figure shows the thermal decomposition in air, and curve 2 (filled circles) refers to a vacuum of ≈ 10 Pa. The minus signs in the weight changes indicate a weight decrease. In curve 1, a small break is seen at around 150°C. The weight decrease was 5% at that temperature. There is no such break in curve 2.

According to the literature [6,7], the dehydration reaction of the octahydrate is thought to proceed via the following steps

$$Nd_2(SO_4)_3 \cdot 8H_2O \rightleftharpoons Nd_2(SO_4)_3 \cdot 5H_2O + 3H_2O \tag{1}$$

$$Nd_2(SO_4)_3 \cdot 5H_2O \rightleftharpoons Nd_2(SO_4)_3 \cdot 2H_2O + 3H_2O \tag{2}$$

$$Nd_2(SO_4)_3 \cdot 2H_2O \rightleftharpoons Nd_2(SO_4)_3 + 2H_2O \tag{3}$$

Our data in Fig. 1 show that the dehydration reaction has finished at ≈ 300°C. The observed weight decrease was 20.04%, which was in good agreement with the theoretical weight decrease of 19.98%. This dehydration temperature is comparable with the reported temperature of 250°C [7] or 290°C [6].

The thermal decomposition of $Nd_2(SO_4)_3$ shown in the following equation

$$Nd_2(SO_4)_3 \rightleftharpoons Nd_2O_2SO_4 + 2SO_2 + O_2 \tag{4}$$

began to proceed at 890°C when the compound was heated in air. In a vacuum, the starting temperature was lowered to 750°C. The above decomposition reaction was finished at 970°C in vacuo but continued up to nearly 1100°C in air. The thermal decomposition of $Nd_2(SO_4)_3$ has been reported as commencing at 890 [8], 927 [9] or 950°C [10]. Our results are in good agreement with these data.

The reaction to form Nd_2O_3 from $Nd_2O_2SO_4$

$$Nd_2O_2SO_4 \rightleftharpoons Nd_2O_3 + SO_2 + 1/2O_2 \tag{5}$$

was observed to start at 1020°C in vacuo, as shown in curve 2 of Fig. 1. With heating in air, however, weight decrease due to this reaction did not occur below 1100°C. These experimental facts show that a higher temperature is required for the decomposition in air. Our result is in line with the published data for the

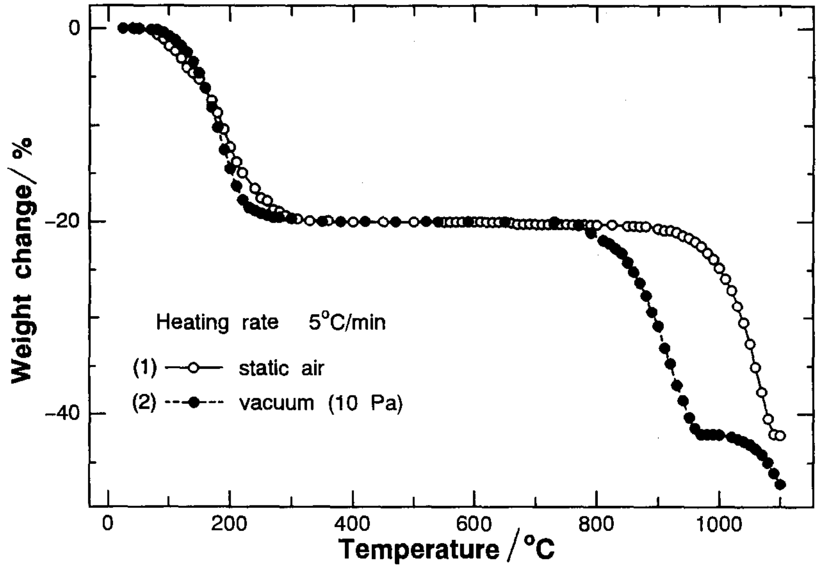

Fig. 1. TG curves of thermal decomposition of $Nd_2(SO_4)_3 \cdot 8H_2O$.

decomposition temperature in air. The values are as high as 1200 [11], 1235 [8] or 1320°C [10].

Suponitskii et al. [12] reported the formation of $Nd_2O_2SO_3$ in a sequence of atmospheric oxidation of Nd_2O_2S, but this compound was not found in this study.

3.2. Reduction of $Nd_2(SO_4)_3$ with annealed carbon

The reaction conditions for the reduction of $Nd_2(SO_4)_3$ with annealed carbon are listed in Table 1. The weight change of run 1 in the table is shown in Fig. 2 as curve 1, and that of run 2 as curve 2. The heating rate for these curves was 5°C min^{-1}. It is seen from the figure that the weight change ratio is slightly larger in the flowing N_2 atmosphere (curve 2) at low temperatures, but at 600°C there is almost no difference between the weight changes in the static and flowing N_2 atmospheres (curves 1 and 2). The starting material, which was a mixture of anhydrous $Nd_2(SO_4)_3$ and annealed carbon, remained unchanged after heating at 600°C, as determined by X-ray diffraction analysis. Hence the weight decrease of 3.9% at 600°C should be ascribed to the moisture absorbed by the annealed carbon during mixing. In order to ascertain this point, two experiments were conducted in which the carbon was heated without $Nd_2(SO_4)_3$ in a stream of N_2. Fig. 3 shows the weight decrease of carbon on heating. In the figure, the solid line (first heating) shows the weight change of the activated carbon. The broken line (second heating) pertaining to the annealed carbon was obtained immediately after the first heating, where dry N_2 was passed through the system throughout the cooling and heating processes.

Table 1
Experimental parameters and products of carbon reduction of $Nd_2(SO_4)_3$ [a]

Run	Carbon	Atmosphere	Nitrogen flow rate in ml min^{-1}	Heating rate in °C min^{-1}	$Nd_2(SO_4)_3$/ carbon mixing ratio in 1 mol^{-1}	Product by X-ray analysis	Amount of sulfide phase in wt%
1	AN	F	0	5	1:20	OS	–
2	AN	F	100	5	1:20	OS	–
3	AN	F	170	5	1:20	OS	–
4	AN	F	500	5	1:20	OS	–
5	AN	E	100	10	1:20	OS	–
6	AC	F	0	5	1:20	OS	–
7	AC	F	100	5	1:20	OS + S	16
8	AC	F	100	10	1:20	OS + S	38
9	AC	E	0	10	1:20	OS + S	29
10	AC	E	100	5	1:20	OS + S	30
11	AC	E	100	10	1:20	OS + S	33
12	AC	E	500	10	1:20	OS + S	46
13	AC	E	100	15	1:20	OS + S	48
14	AC	E	100	15	1:50	OS + S	58
15	AC	E	100	15	1:100	OS + S	28

[a] AC = activated carbon; AN = annealed carbon; E = evacuated to ≈1300 Pa and refilled with nitrogen before heating; F = flushed by nitrogen (0.5 l min^{-1}) for 15 min before heating; OS = neodymium oxysulfide Nd_2O_2S; S = neodymium sulfide.

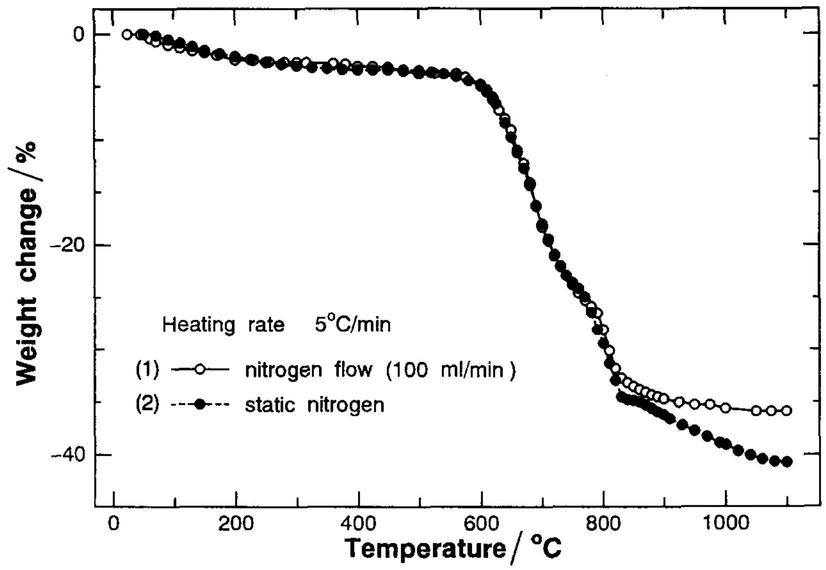

Fig. 2. TG curves of reduction of anhydrous $Nd_2(SO_4)_3$ by annealed carbon.

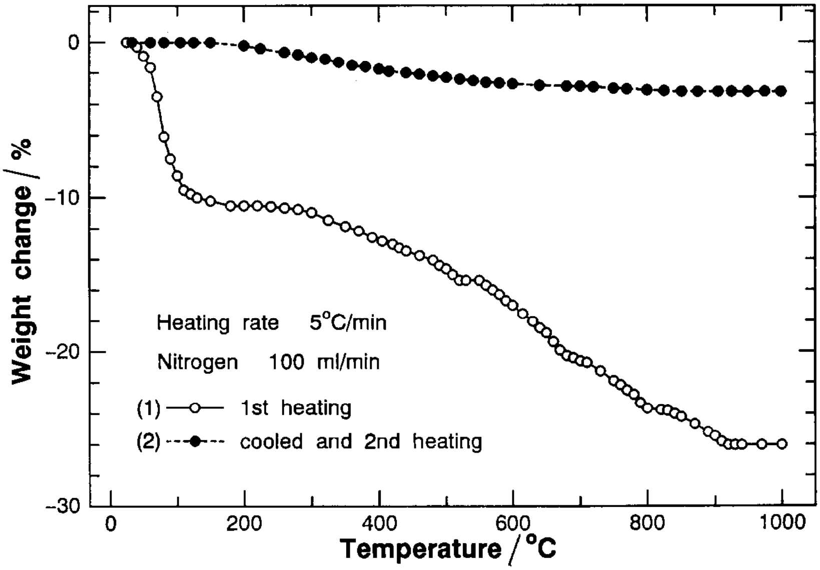

Fig. 3. TG curves of carbon in a flow of N_2.

As seen from Fig. 3, the annealed carbon has lost 2.7% of its weight by 600°C, which is much smaller than the weight decrease of activated carbon. The value of 2.7% corresponds to 0.8% of a mixture of $Nd_2(SO_4)_3$ and annealed carbon for which the mixing mole ratio was 1:20. The difference between 3.9% and 0.8% is therefore considered to be due to the moisture absorbed by the annealed carbon during mixing with $Nd_2(SO_4)_3$. We note that there was no weight change for $Nd_2(SO_4)_3$ during grinding.

It is seen from Fig. 2 that the reduction proceeds in two steps above 600°C. The first reaction takes place at a significant rate between 600 and 800°C, and the second does so between 800 and 880°C. Above 880°C, another distinct weight decrease was observed for the specimen heated in static N_2, which is in contrast to the weight change in a flowing N_2 atmosphere in this range of temperatures. The reason for this difference is not clear.

As the products after the first and the second step reactions were identified as $Nd_2O_2SO_4$ and Nd_2O_2S, respectively, by X-ray diffraction analysis, the most probable reaction of each step would be

$$Nd_2(SO_4)_3 + 2C \rightleftharpoons Nd_2O_2SO_4 + 2CO + 2SO_2 \quad \text{(1st step)} \tag{6}$$

$$Nd_2O_2SO_4 + 4C \rightleftharpoons Nd_2O_2S + 4CO \quad \text{(2nd step)} \tag{7}$$

Hence the overall reaction becomes

$$Nd_2(SO_4)_3 + 6C \rightleftharpoons Nd_2O_2S + 6CO + 2SO_2 \tag{8}$$

The sample before heating was a mixture of 1 mmol of $Nd_2(SO_4)_3$ and 20 mmol of annealed carbon. Then the calculated weight decrease of reaction (6) is 22.54%

Table 2
Weight changes of a mixture of 1 mmol of $Nd_2(SO_4)_3$ and 20 mmol of carbon when heated in N_2

Region of temperature	Weight change W in wt%			
	Annealed carbon		Activated carbon	
	Static N_2 Run 1	N_2 flow Run 2	Static N_2 Run 6	N_2 flow Run 7
RT-600°C	3.63	3.65	3.78	3.78
600-800°C	22.28	21.72	20.30	20.22
800-880°C	11.18	11.18	10.84	11.70

and that of reaction (7) is 13.71%. Table 2 shows the weight decrease (wt%) in the three regions of temperatures. The observed weight decrease for reaction (6) was 22.28 and 21.72% in static N_2 and flowing N_2, respectively. These values are a little smaller than the calculated values. The same can be said also for reaction (7). Such differences could be explained if a part of the CO was further oxidized to CO_2 in the above reactions. In this case, the overall reaction should be replaced by

$$Nd_2(SO_4)_3 + (6-p)C \rightleftharpoons Nd_2O_2S + (6-2p)CO + pCO_2 + 2SO_2 \tag{9}$$

where the p value can be $0 < p < 3$. Eq. (9) leads to

$$\Delta W = 36.26 - 1.47p \tag{10}$$

where ΔW represents the weight decrease in wt%. As the observed ΔW value was 33%, the p value is calculated as being ≈ 2.2, i.e. $CO/CO_2 = 0.73$.

In the case in which H_2 is used as the reducing agent of $Nd_2(SO_4)_3$, the product is Nd_2O_2S in the temperature range between 600 and 650°C [13,14]. In our work, where carbon was used, $Nd_2O_2SO_4$ was formed in this range of temperature and Nd_2O_2S was produced at temperatures above 800°C. The reducing power of H_2 seems to be stronger at such low temperatures.

3.3. Reduction of $Nd_2(SO_4)_3$ with activated carbon

The reaction conditions with activated carbon are shown in Table 1. Fig. 4 indicates the weight change for runs 6 and 7 in the table as curves 1 and 2, respectively. The heating rate, 5°C min^{-1}, was the same as that for Fig. 2. As above, the reaction of the mixture of 1 mmol of $Nd_2(SO_4)_3$ and 20 mmol of carbon was studied. In Fig. 4, both curves 1 and 2 below 600°C showed a slightly larger weight change than those with annealed carbon. It is a feature of the two curves of Fig. 4 that they almost coincide, showing that whether the N_2 is flowing or not is unimportant in this range of temperatures. At 600°C, the observed weight decrease in Fig. 4 is 5%. This value is reasonable because, in Fig. 3, the curve of the first heating (activated carbon) showed a 17% decrease by 600°C which corresponds to a 5.0% weight decrease for this mixture.

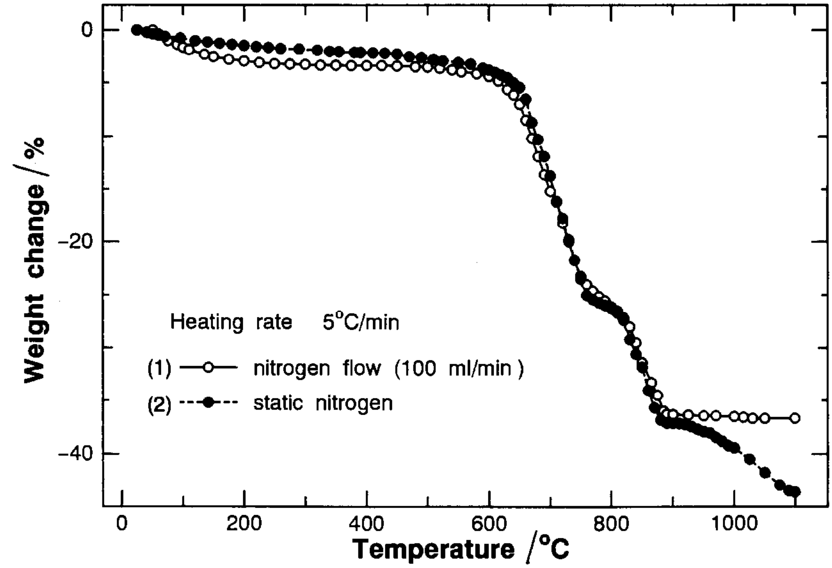

Fig. 4. TG curves of reduction of anhydrous $Nd_2(SO_4)_3$ by activated carbon.

The reaction above 600°C also proceeds in two steps as shown in Fig. 4. The weight decreases listed in Table 2 are, however, smaller than those observed in the reaction with annealed carbon. By X-ray diffraction analysis, the reaction products were identified as $Nd_2O_2SO_4$ and a mixture of Nd_2O_2S and Nd_3S_4 after the first and the second reaction steps respectively. The above experimental results suggest the following reaction

$$\begin{aligned} Nd_2(SO_4)_3 + \left(6+\frac{16}{3}q-r\right)C &\rightleftharpoons (1-q)Nd_2O_2S+\frac{2}{3}qNd_3S_4 \\ &+\left(6+\frac{16}{3}q-2r\right)CO+rCO_2+\left(2-\frac{5}{3}q\right)SO_2 \qquad (11) \end{aligned}$$

In this case the weight decrease (wt%) becomes

$$\Delta W = 36.26 + 5.22q - 1.47r \qquad (12)$$

where q and r represent the amounts of Nd_3S_4 and CO_2 respectively. Eq. (12) shows that the formation of Nd_3S_4 causes a larger decrease in weight whereas that of CO_2 suppresses this effect.

Here, we consider the larger weight decrease of activated carbon itself during heating. As is seen from Fig. 3, activated carbon has a weight loss of 17% below 600°C and ≈9% between 600 and 1000°C. The latter value causes a weight decrease of 2.6% in the mixture of $Nd(SO_4)_3$ and carbon, which is no longer negligibly small, unlike the annealed carbon (Table 2). The overall weight change in the reaction of $Nd_2(SO_4)_3$ with activated carbon between 600 and 880°C becomes 28.54 and 29.32% in static and flowing N_2, respectively. These values are considerably smaller than those with annealed carbon, i.e. 33.46 and 32.90%.

The materials vaporized from the activated carbon on heating in N_2 are assumed to consist of moisture and volatile hydrocarbons [15]. The hydrocarbons not only cause the difference between the calculated and the observed weight changes but also play an important role in lowering the reaction temperatures by ≈ 50°C. If $Nd_2(SO_4)_3$ is also reduced by the hydrogen in such hydrocarbons, the overall reaction will become

$$Nd_2(SO_4)_3 + \left(6 + \frac{16}{3}q - s - t\right)C + 2tH \rightleftharpoons (1-q)Nd_2O_2S + \frac{2}{3}qNd_3S_4$$
$$+ \left(6 + \frac{16}{3}q - 2s - t\right)CO + sCO_2 + \left(2 - \frac{5}{3}q\right)SO_2 + tH_2O \qquad (13)$$

and

$$\Delta W(\text{wt\%}) = 36.26 + 5.22q - 1.47s - 1.22t \qquad (14)$$

where s and t stand for the amounts of CO_2 and H_2O vapour evolved, respectively.

The Nd_3S_4 ratio in the product was estimated using a calibration curve which gave the Nd_3S_4/Nd_2O_2S ratio as a function of the integrated X-ray peak intensities. The Nd_3S_4 used for constructing the curve was prepared by reducing $Nd_2(SO_4)_3$ with CS_2 at 1300°C, which is well above the α–γ transformation temperature, namely, 1177°C [16] or 1222°C [17]. The composition of this cubic γ-phase compound, γ-Nd_2S_{3-x}, was close to Nd_3S_4, showing almost the same lattice parameter $a = 0.8526(2)$ nm [18]. The peak positions and intensities of Nd_3S_4 and γ-Nd_2S_{3-x} were very close, as shown in Fig. 5. These intensities are in good agreement with those calculated using the LAZY PULVERIX program, as tabulated in Table 3.

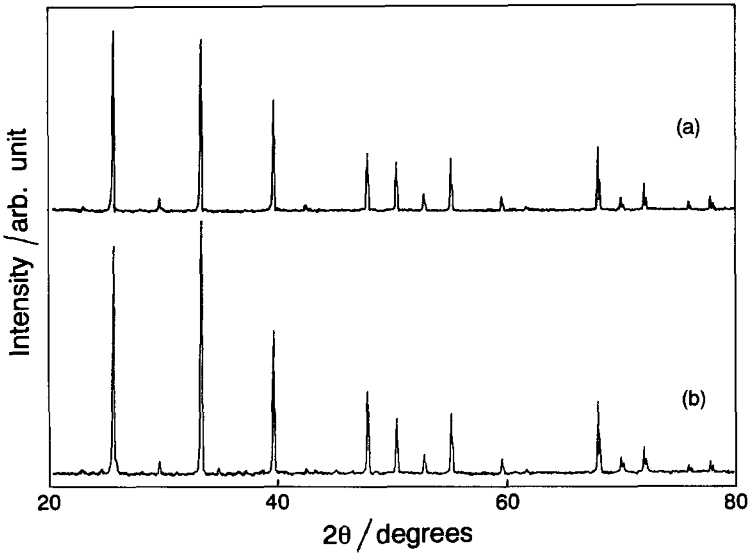

Fig. 5. X-ray diffraction patterns of γ-Nd_2S_{3-x} and Nd_3S_4. (a) γ-Nd_2S_{3-x}, (b) Nd_3S_4.

Table 3
Calculated X-ray intensities for γ-Nd_2S_3 and Nd_3S_4 [a]

h	*k*	*l*	Intensity		*h*	*k*	*l*	Intensity	
			Nd_2S_3	Nd_3S_4				Nd_2S_3	Nd_3S_4
2	1	1	87.4	99.7	5	4	1	14.7	15.0
2	2	0	6.5	7.9	6	3	1	4.3	4.5
3	1	0	100.0	100.0	4	4	4	7.5	7.8
3	2	1	61.5	61.4	5	4	3	0.4	0.3
4	0	0	1.7	1.9	7	1	0	0.2	0.2
4	2	0	38.0	40.4	6	4	0	8.0	8.5
3	3	2	24.6	26.1	6	3	3	6.4	6.7
4	2	2	8.6	8.7	5	5	2	6.1	6.4
5	1	0	5.4	6.4	7	2	1	13.7	14.3
4	3	1	23.0	24.4	6	4	2	5.2	5.3
5	2	1	7.3	8.1	7	3	0	1.5	1.8
4	4	0	1.8	2.0	6	5	1	3.7	3.9
5	3	0	0.3	0.3	7	3	2	1.5	1.7
5	3	2	21.0	22.1	8	0	0	1.8	2.1
6	1	1	14.9	15.1	7	4	1	0.3	0.2
6	2	0	7.5	7.3	6	5	3	6.9	7.5

[a] Space group $I\bar{4}3d$ (No. 220); occupancy factor of Nd (12a): 0.889 for Nd_2S_3 and 1.000 for Nd_3S_4; position parameter of S (16c): $x = 0.074$ *; no temperature factors were used. * No values reported for Nd_2S_3 or Nd_3S_4; this is an estimated value from the other lanthanide sesquisulfides: 0.0739 for La_2S_3 [19], 0.073 for Ce_2S_3 [20], 0.0716–0.07237 for $Sm_{2.71}S_4$–$Sm_{3.05}S_4$ [21].

The amount of the Nd_3S_4 phase so determined varied from 16% (this value corresponds to $q = 0.22$ in Eq. (13)) to 58% ($q = 0.67$) according to the reaction conditions (Table 1). If we take $q = 0.3$ and regard the CO/CO_2 ratio as 0.73 from the p value of Eq. (10), Eq. (14) is expressed as

$$\Delta W = 28.53 + 1.87s \tag{15}$$

With the experimental data of Table 2 for the flowing N_2 condition (Run 1), i.e. 31.92%, the above equation yields $s = 1.32$, which leads to 5.3% as the weight of the carbon and hydrogen used for reaction (13). The contribution of hydrocarbons is less than 49%.

Moskalenko et al. [14] obtained Nd_2O_2S by reducing $Nd_2(SO_4)_3$ in natural gas at temperatures of 600–650°C. This product is not the same as that in this experiment, i.e. $Nd_2O_2SO_4$ in the same range of the temperatures. This may be because our work involved a solid–solid reaction, in contrast to their gas–solid reaction.

3.4. *Effect of $Nd_2(SO_4)_3$ and carbon mole ratio*

The effect of the $Nd_2(SO_4)_3$-to-carbon mole ratio on the reaction is summarized in Table 4. There is no large difference in the reactions at a mole ratio of 1:20 or

Table 4
Effect of $Nd_2(SO_4)_3$-to-carbon mole ratio. Heating rate 5°C min^{-1}, nitrogen flow rate 100 ml min^{-1}

	$Nd_2(SO_4)_3$-to-C ratio					
	Annealed carbon			Activated carbon		
	1:16	1:12	1:20	1:6	1:12	1:20
Wt. decrease in wt%						
Rt–600°C	2.71	1.88	3.65	4.75	4.62	3.78
600–880°C	40.75	37.33	32.90	39.52	36.67	31.92
Calc. wt. decrease, reaction (8)	45.66	41.09	36.26	45.66	41.09	36.26
p value of reaction (9)	(2.7)	2.3	2.3	3.3	–	–
s value of reaction (13)	–	–	–	(1.5)	2.0	1.8
Product (X-ray analysis) [b]	OS + SA(?)	OS	OS	OS	OS + S	OS + S

[a] With $p = 0.3$, $(6 + \frac{16}{3}q - 2s - t)/s = 0.73$. [b] OS = Nd_2O_2S: SA = $Nd_2O_2SO_4$: S = N_3S_4.

1:12 for annealed carbon and activated carbon. In the case of annealed carbon, the product after heating at 1100°C was Nd_2O_2S in each case, and also the p values of reaction (9) were the same. For activated carbon, the product in each case was a mixture of Nd_2O_2S and Nd_3S_4, with s values of 1.8 and 2.0 as listed in the table.

On the other hand, if the mole ratio was lowered to 1:6, several additional weak lines were observed in the X-ray diffraction pattern of the products of reaction with annealed carbon. These lines appeared to be from $Nd_2O_2SO_4$. The p value of 2.7 is somewhat discrepant from $p = 2.3$ for the mixing ratios 1:20 and 1:12.

The difference is much larger with the mole ratio 1:6 products from activated carbon. As shown in Table 4, the sole product was Nd_2O_2S, i.e. no Nd_3S_4 was formed in admixture with Nd_2O_2S. The s value of 1.5 was smaller than those for mole ratios 1:20 and 1:12. The above experimental results show that a mole ratio of 1:12 is sufficiently high but 1:6 is too low to produce Nd_3S_4.

3.5. *Effect of evacuation*

As shown in Table 1, a series of experiments was carried out by evacuating the system to ≈ 1300 Pa and refilling with N_2 before heating. This process seemed to have some effect in enhancing the proportion of the sulfide phase in the product mixtures when the heating rate was low (5°C min^{-1}). The effect of reducing the pressure below 1300 Pa was then examined by using pellets which had been prepared with the addition of a small amount of organic lubricant. In this pelletized form, the carbon did not spatter during evacuation to these lower pressures. The experiments were carried out for the samples with a mole ratio of $Nd_2(SO_4)_3$ to activated carbon of 1:20. The system was evacuated to 1 Pa and refilled with N_2 to ambient pressure before heating. The heating rate was 5°C min^{-1} and the N_2 flow rate during heating was 100 ml min^{-1}.

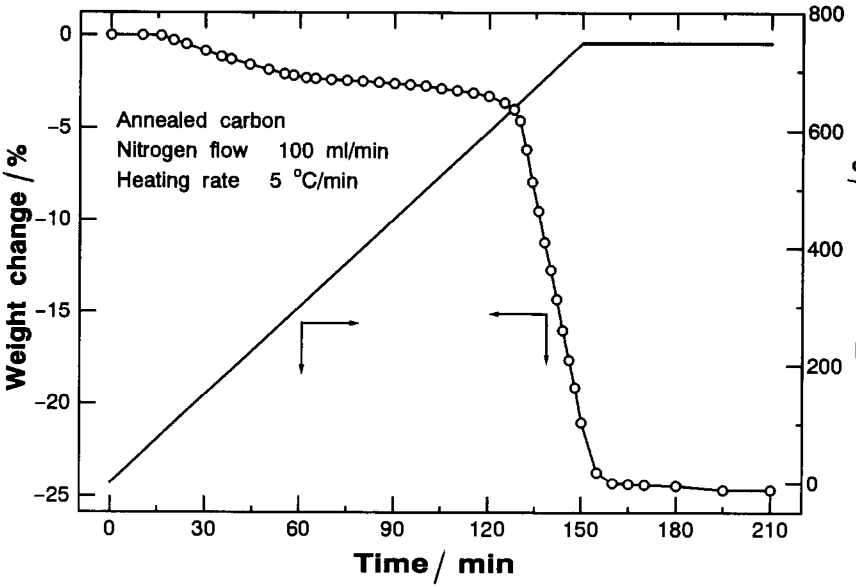

Fig. 6. TG curve of reduction of anhydrous $Nd_2(SO_4)_3$ with annealed carbon in holding mode.

The result showed that the total weight decrease in the temperature range 500–880°C was 57.21 wt%. After correction for evaporation of lubricant the value changed to 32.47 wt%, which is comparable with the weight decrease of 31.92 wt% observed when the system was evacuated to 1300 Pa. The product established by X-ray diffraction analysis was a mixture of Nd_2O_2S and Nd_3S_4. No clear difference was observed in the X-ray peak intensities of these two phases. It can be concluded that evacuation to a higher vacuum of 1 Pa has no significant effect on the reaction compared with a vacuum of 1300 Pa.

3.6. Holding mode experiments

Additional experiments were carried out in a holding mode: the sample was heated to a selected temperature (700 or 750°C) and held at that temperature for 1 h. The TG curve of the experiment with annealed carbon is shown in Fig. 6. The weight was almost unchanged during the holding period, showing that the heating rate of 5°C min^{-1} was low enough for reaction at these temperatures. Similar experiments were carried out with activated carbon in this mode. The product as established by X-ray diffraction analysis was $Nd_2O_2SO_4$ after heating with annealed carbon (Fig. 6). In contrast to this result, a mixture of $Nd_2O_2SO_4$ and Nd_2O_2S was formed with activated carbon at 700°C, and Nd_2O_2S resulted after heating at 750°C. These results show that reaction (7) proceeds at lower temperatures with activated carbon. As the sulfide phase was not observed to form in this temperature range (700–750°C), the formation reaction of Nd_3S_4 is considered to occur at higher temperatures.

Acknowledgement

One of the authors (M.Sk.) is deeply grateful to MONBUSHO (Japanese Ministry of Education, Culture and Science) for scholarship support.

References

[1] M.W. Shafer, Mater. Res. Bull., 7 (1972) 603.

[2] A.A. Eliseev, A.A. Grizik, N.N. Borzenkov, G.P. Borodulenko, N.M. Gracheva, V.V. Evdokimova and V.I. Novokshonov, Zh. Neorg. Khim., 23 (1978) 2622.

[3] E.D. Eastman, L. Brewer, L.A. Bromley, P.W. Gilles and N.L. Lofgren, J. Am. Chem. Soc., 72 (1950) 2248.

[4] J.P. Dismukes and J.G. White, Inorg. Chem., 3 (1964) 1220.

[5] K. Yvon, W. Jeitschko and E. Parthe, J. Appl. Crystallogr., 10 (1977) 73.

[6] W.W. Wendlandt, J. Inorg. Nucl. Chem., 7 (1958) 51.

[7] A. Saito, Thermochim. Acta, 124 (1988) 217.

[8] M.W. Nathans and W.W. Wendlandt, J. Inorg. Nucl. Chem., 24 (1962) 869.

[9] V.I. Laptev, J.L. Suponitskii and A.F. Vorobev, Zh. Neorg. Khim., 32 (1987) 547.

[10] A.N. Pokrovskii and L.M. Kovba, Zh. Neorg. Khim., 21 (1976) 567.

[11] E.V. Margulis, M.M. Shokarev, V.N. Novoselova and F.I. Vershinina, Zh. Neorg. Khim., 15 (1970) 1451.

[12] J.L. Suponitskii, V.I. Laptev and A.F. Vorobev, Zh. Neorg. Khim., 34 (1989) 2690.

[13] V.I. Laptev, J.L. Suponitskii and A.F. Vorobev, Zh. Neorg. Khim., 27 (1982) 1935.

[14] V.I. Moskalenko, A.K. Molodkin, V.G. Remizov, J.E. Bogatev and M.B. Varfolomeev, Zh. Neorg. Khim. 25 (1980) 1698.

[15] E.G.Doying, in H.F. Mark, J.J. McKeita, Jr. and D.F. Othmer (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 4, Interscience, New York, 1964, p. 149.

[16] O.V. Andreev, T.M. Kislovskaya and A.V. Kertman, Zh. Neorg. Khim., 35 (1990) 1280.

[17] P. Besançon, J. Solid State Chem., 7 (1973) 232.

[18] V. van Tien and P. Khodadad, Bull. Soc. Chim. Fr., 1 (1969) 30.

[19] N.V. Podberezskaya, N.V. Kozhemyak, L.G. Golubeva, V.P. Balko, V.V. Bakanin and S.V. Borisov, J. Struct. Chem. USSR (Engl. Transl.), 20 (1979) 931.

[20] M. Atoji, J. Chem. Phys., 54 (1971) 3226.

[21] B. Anselment, H. Barnighausen and M. Eitel, J. Less-Common Met., 116 (1986) 1.