STUDY ON TECHNOLOGY FOR PREPARATION OF METALLIC DYSPROSIUM FROM THE OXIDE BY METALLOTHERMIC REDUCTION METHOD

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Abstract

The studies on technology for preparation of metallic dysprosium from the oxide by metallothermic reduction method were reported in this work. The fluorination of dysprosium oxide (Dy_2O_3) by ammonium bifluoride (NH_4HF_2) to prepare anhydrous dysprosium fluoride was implemented. The temperatures of the fluorination determined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) ranged from 350°C to 450°C. Energy-dispersive X-ray spectroscopy (EDS) method was used to analyze the elemental composition in the as-prepared products; the fluorine (F_2) and dysprosium (Dy) elemental composition calculated from the [DyF_3] formula are in good agreement with those calculated from the EDS pattern. The anhydrous oxygen-free dysprosium fluoride was used to study the preparation of metallic dysprosium by the calcinothermic reduction method. The parameters of the calcinothermic process were temperature, time and ratio of calcium to anhydrous DyF_3. The metallic dysprosium of >96% was obtained from the processes.

Keywords: anhydrous dysprosium fluoride, fluorination, calcinothermic reduction, metallic dysprosium.

1. Introduction

Dysprosium (Dy) is one of valuable heavy rare earth elements. It is one of the components of Terfenol-D ($Tb_xDy_{1-x}Fe_2$; x=~0.3), along with iron and terbium, of high energy Nd-Fe-B ($Nd_{13.4-x}Dy_{0.2+x}Fe_{79.7}M_{0.4}B_6$; x=0-0.3; M is Al or Ga, Co, Cu) permanent magnets. Terfenol-D has the highest room-temperature magnetostriction of any known material, which is employed in transducers, wide-band mechanical resonators, and high-precision liquid-fuel injectors. Modern electrical generators and motors for hybrid and electric vehicles, wind turbine generators or hard disc drives require dysprosium. Nearly 95% of the total Dy demand accounts for the use in permanent magnets. In addition, Dy has a high thermal-neutron absorption cross-section; therefore, dysprosium-oxide-nickel cermets are used in neutron-absorbing control rods in nuclear reactors. Dy is used in dosimeters for measuring ionizing radiation [1-3]

There are two main techniques to prepare rare earth metals, namely molten salt electrolysis and metallothermic reduction. Both techniques use anhydrous chloride or fluoride rare earth salts as feed materials. However, the disadvantage of chloride rare earth salts is their highly hygroscopic property; moreover, fluoride rare earth salts overcome this problem; therefore, these salts are preferred for the preparation of metallic rare earths [4]. Depending on the properties of the metallic rare earth melting points, either molten salt electrolysis or metallothermic reduction techniques are applied for the preparation of the metallic rare earths. Molten salt electrolysis is applied popularly for the preparation of light rare earth metals, such as lanthanum (La), cerium (Ce), praseodymium (Pr) and neodymium

(Nd), because they have low melting points of less than 1100°C [5-8]. The melting points of dysprosium (1407°C) is high; therefore, molten salt electrolysis is not applied, and the metallothermic reduction method is popularly used to produce these metals [2-3]. Thus, the production of rare earth metals by rare earth fluoride molten salt electrolysis or metallothermic reduction techniques involves two main steps: (i) preparation of anhydrous fluoride, for example dysprosium fluoride from their compounds, such as dysprosium oxide; and (ii) rare earth fluoride molten salt electrolysis or calcinothermic reduction of anhydrous oxygen-free dysprosium fluoride into metallic dysprosium [9-11].

Yen Phu and Ben Den rare earth mines are two of the highly promising rare earth resources in Vietnam; they include Dong Pao and Nam Xe (bastnaesite), Muong Hum (monazite), Yen Phu (xenotime) and Ben Den (ion adsorption clay). The Yen Phu and Ben Den mines are rich in high-value commercial rare earths, especially dysprosium, terbium and yttrium. The contents of neodymium, terbium, dysprosium and yttrium in the Yen Phu total rare earth oxides (TREO) are 13.8%, 0.6%, 3.1% and 31%, respectively, and the contents of these rare earths in the Ben Den TREO are 22.5%, 0.5%, 2.7% and 0,5%, respectively [12-14]. Therefore, research on the comprehensive processing of Yen Phu xenotime and Ben Den ion adsorption clay to attain commercially valuable rare earths, such as terbium and dysprosium, is necessary and important.

This study carried out the metallic Dy preparation by calcinothermic reduction of DyF_3. The anhydrous Dy fluoride and metallic Dy preparational parameters such as molar ratios, temperature, and run time have been studied and discussed.

2. Experimental

Dy compound used in this study is pure dysprosium oxide (Dy_2O_3) prepared from $DyCl_3$ solution from Yen Phu xenotime concentrate processing in Institute for Technology of Radioactive and Rare Elements (ITRRE) [12-14]; chemicals such as Ca, ammonium bifluoride (NH_4HF_2), hydrofluoric (HF) acid, etc. are pure ones.

Two vacuum tube furnace were self-made, one of these has maximum operating temperature of 1000°C that is used for the preparation of anhydrous DyF_3 and the other has maximum operating temperature of 1600°C that is used for calcinothermic reduction of DyF_3 and cast to prepare metallic Dy.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using a SETARAM Thermal Analyzer were used to determine the temperature range of Dy_2O_3 fluorination by NH_4HF_2. The phase purity of the as-prepared products was identified by X-ray diffraction (XRD) using a SIEMENS D5005 instrument with monochromatized Cu Kα radiation ($\lambda = 0.15418$ nm). The elemental composition in the fluorinated samples was determined by the energy-dispersive X-ray spectroscopy (EDS) method using a JEOL JSM-IT100LV instrument. Dy content in the calcilothermic samples were analyzed by ICP-OES (Horiba, Japan).

3. Results and discussions

3.1. Study on the fluorination of Dy_2O_3 by NH_4HF_2 to prepare the anhydrous Dy fluoride

The studies on the preparation of anhydrous DyF_3 were implemented. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to determine the temperature arrange of the Dy_2O_3 fluorination by NH_4HF_2 (Fig. 1). A mixture of ammonium bifluoride with dysprosium oxide containing NH_4HF_2 and Dy_2O_3 in Dy^{3+}/NH_4^+ mole ratio of 1/3.5 was analyzed by DTA-TGA. The results indicated that the fluorination temperature is at more than 250°C. Based on this mass variation let's assume that the fluorination can proceed through two following reactions:

$$Dy_2O_3 + 4NH_4HF_2 = 2DyF_3 \cdot NH_4F + 2NH_3\uparrow + 3H_2O\uparrow$$

$$DyF_3 \cdot NH_4F = DyF_3 + NH_4F\uparrow$$
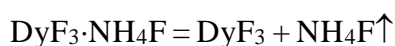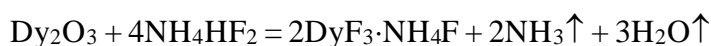
Some studies on fluorination of rare earths oxides (Y_2O_3, Nd_2O_3) by ammonium bifluoride to prepare anhydrous rare earths fluoride (YF_3, NdF_3) were reported the formation of the analogous intermediate compound ($NH_4Y_2F_7$, NH_4NdF_4) at a temperature of 200-250°C. The conversion of $NH_4Y_2F_7$ into YF_3 and NH_4NdF_4 into NdF_3 occur at temperatures in excess of 350°C [15-19].
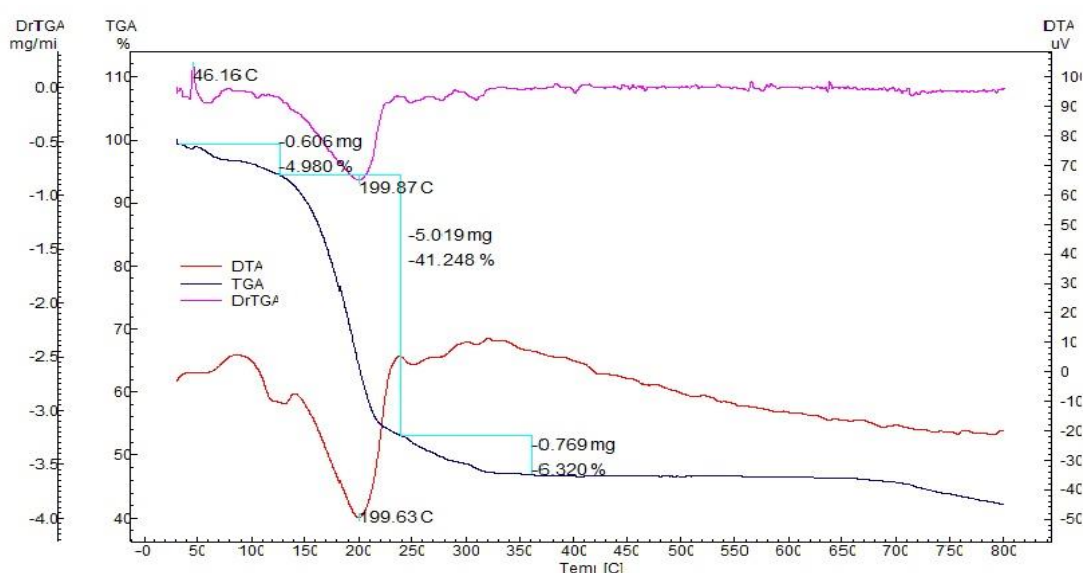

Fig. 1. The DTA and TGA curves of the Dy_2O_3 and NH_4HF_2 mixture.

Based on the thermal analysis, the fluorination temperature range was determined from 350 to 450°C; and the studies were carried out at these temperatures for 1-3hrs. Fig. 2 showed the XRD spectrum of the fluorinated sample at 450°C; the result indicated the pure phase of DyF_3 was formed. Element composition in the fluorinated samples was identified by EDS method. Table 1 and Fig. 3 showed element composition and the EDS pattern of DyF_3.

Table 1. The element composition of DyF_3 at fluorination temperature/ time.

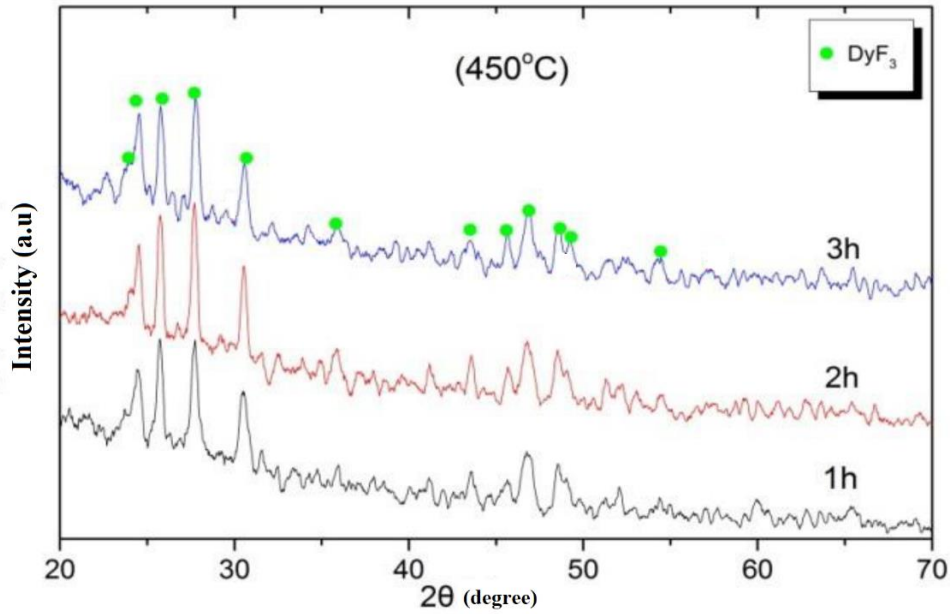| Element	Element composition (%)				
	350°C/3 h	*450°C/1 h*	*450°C/2 h*	*450°C/3 h*	*DyF₃*
Dy	31	27	29	31	31
F	69	73	71	69	69
Ratio of F/Dy	2,23	2,70	2,45	2,23	2,23

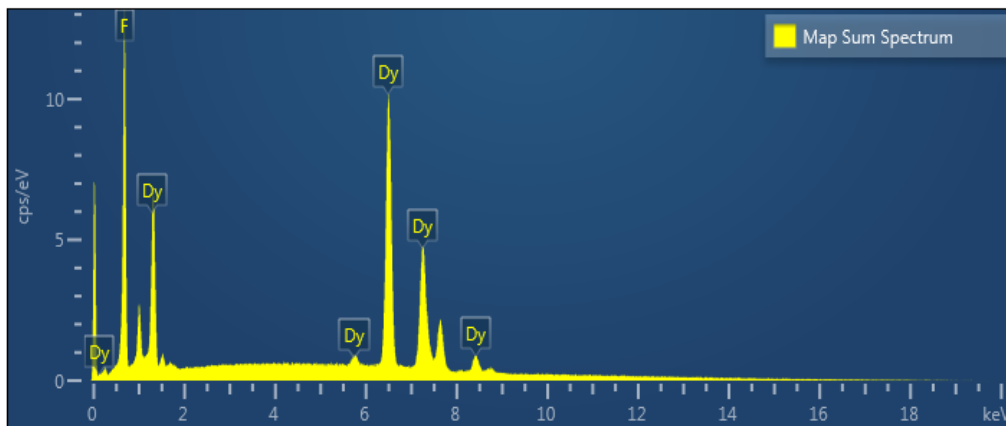**Fig. 2.** The XRD spectrum of of the fluorinated sample at 450°C.

Fig. 3. The EDS pattern of DyF$_3$.

As shown in Fig. 3 and Table 1, there is not any peak of oxygen element in the EDS pattern, and the F and Dy elemental compositions calculated from the [DyF$_3$] formula are in good agreement with those calculated from the EDS result. The above results indicated that optimum parameters for the preparation of anhydrous DyF$_3$ were: fluorination temperature and time of 350-450°C and 3h, respectively [20]. The anhydrous DyF$_3$ is used as a raw material for the calcinothermic reduction to prepare the metallic Dy.

3.2. Study on the calcinothermic reduction of DyF$_3$ to prepare the metallic dysprosium

The studies on the calcinothermic reduction wese conducted. There are three factors affecting on the calcinothermic reduction of DyF$_3$, including calcinothermic temperature and time, and molar ratio of Ca/DyF$_3$. The response surface methodology (RSM) based on a central composite face-centered (CCF) design was empirically used to model the interactive effect of the independent variables on the dependent response. The calcinothermic reduction yield (Y, %) was considered the

dependent response, and the temperature (X_1, °C), Ca/DyF$_3$ molar ratio (X_2, mol/mol), and time (X_3, h) were considered independent variables (factors). The variables' levels in coded and actual values are presented in Table 2. The total number of required experimental runs was $2^k+2k+n_0=15$, where k is the number of factors (k=3) and n_0 is the number of replications at the center points ($n_0=1$). Experimental matrix in the planning experimental region is also presented in Table 2. The CCF regression model can be described in the form given in Eq. (1).

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i,j=1(i \neq j)}^{k} b_{ij} X_i X_j , \tag{1}$$

Where: Y is the dependent response;

b_0 is the constant coefficient; b_i, b_{ii} and b_{ij} are the linear, quadratic, and interaction coefficients, respectively;

X_i and X_j are the coded values of the independent variables; $X_i X_j$ and X_i^2 represent the interaction and quadratic terms, respectively.

The experimental studies were determined the planning experimental region, including the temperature X_1 of 1400 – 1500°C, Ca/DyF$_3$ molar ratio X_2 of 1.95 – 2.25 and time X_3 of 0.5 – 1h. The effects of the independent variables on the dependent response were studied based on a CCF design. The results of 15 experimental runs are presented in Table 2. The results were also entered into the MODDE 5.0 software to determine the model by multiple linear regressions. The final calculated equation for the calcinothermic reduction of DyF$_3$ to prepare metallic Dy is:

$$Y=84,34+2,21X_1+2,95X_2+1,22X_3-3,47X_1^2-1,97X_2^2-0,62X_3^2+0,11X_1X_2-0,01X_1X_3-0,39X_2X_3 \tag{2}$$

Table 2. Central composite rotatable design arrangement and results.

Run	Independent variables (X_i)						Responses (Y)	
	Coded levels			Real values			Experimental in %	Calculated in %
	X_1	X_2	X_3	X_1	X_2	X_3		
1	-1	-1	-1	1400	1.95	0.5	71.4	71.60359
2	1	-1	-1	1500	1.95	0.5	75.3	75.82360
3	-1	1	-1	1400	2.25	0.5	78.1	78.05364
4	1	1	-1	1500	2.25	0.5	82.7	82.72362
5	-1	-1	1	1400	1.95	1	74.8	74.84360
6	1	-1	1	1500	1.95	1	78.9	79.01362
7	-1	1	1	1400	2.25	1	80.2	79.74362
8	1	1	1	1500	2.25	1	84.5	84.36361
9	-1	0	0	1400	2.1	0.75	78.4	78.65558
10	1	0	0	1500	2.1	0.75	83.6	83.07558
11	0	-1	0	1450	1.95	0.75	80.3	79.41556
12	0	1	0	1450	2.25	0.75	84.7	85.31558
13	0	0	-1	1450	2.1	0.5	83.2	82.49556
14	0	0	1	1450	2.1	1	84.5	84.93556
15	0	0	0	1450	2.1	0.75	83.8	84.33780

Based on the proposed model (Eq. 2) and considering the energy consumption, low chemical consumption, further waste treatment, and better calcinothermic reduction yield, the factors affecting on the calcinothermic reduction of DyF$_3$ were optimized as follows: the reduction temperature and time are 1450-1460°C and 50 min., respectively, and the Ca/DyF$_3$ molar ratio is 2.15.

Purity of metallic Dy product obtained from the above calcinothermic reduction is ~90%; so the cast processes need to be done to obtain the product of high purity ≥ 95%. The experimental studies on effect of factors, namely content of melting supportant CaCl$_2$ and, temperature and time on the cast process were conducted and the results shown that the optimum parameters for the cast process are: content of melting supportant CaCl$_2$ of 5-6 wt.% and, temperature and time of 1460-1500°C and 60 min. A flowsheet for the metallic Dy preparation from the oxide was established from the above results (presented in Fig. 4).
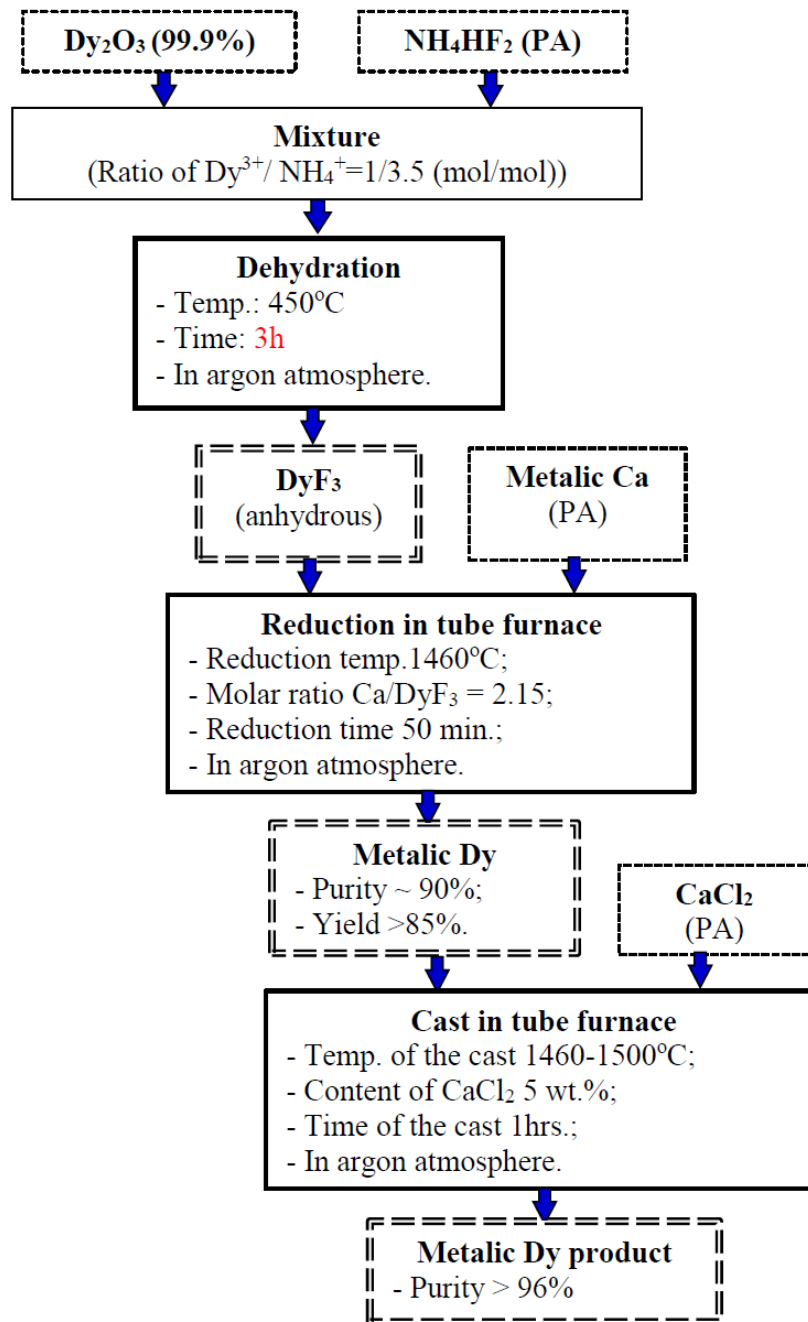

Fig. 4. The flowsheet for the metallic Dy preparation from the oxide.

Conclusions

The fluorination of dysprosium oxide by ammonium bifluoride and its characterization were studied. The optimum parameters for the fluorination of dysprosium oxide by ammonium bifluoride were determined, including a fluorination temperature of 350-450°C with for 3 hrs to attain anhydrous, oxygen-free dysprosium fluoride that can be used to study the preparation of metallic dysprosium by the calcinothermic reduction method.

The preparation of the metallic dysprosium of >95% using two-stage calcinothermic reduction followed by casting was studied. For the calcinothermic reduction, the optimum parameters are as follows: the reduction temperature and time are 1450-1460°C and 50 min., respectively, and the Ca/DyF$_3$ molar ratio is 2.15; for the casting, the optimum parameters are: content of melting suppotant CaCl$_2$ of 5-6 wt.% and, temperature and time of 1460-1500°C and 60 min, respectively.

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