A study of the reduction of dysprosium oxide with lanthanum as a method for producing high purity dysprosium metal

by

Brian Lee Sanden

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ABSTRACT

An investigation was carried out to evaluate the preparation of dysprosium metal by a reduction-distillation method. Lanthanum metal was used as the reductant.

Maximum yields of the as-reduced metal were typically 70 to 75% when a reduction temperature of 1650°C was used. If the reaction was run long enough to obtain a 50% of theoretical yield a purer product was obtained in a much shorter length of time. The yield did not improve when a reduction was performed at 1750°C.

The yield of dysprosium metal was rather insensitive to the amount of excess lanthanum reductant used. A 10% stoichiometric excess of lanthanum was found to give optimum yields, with no further increase in yield when 20 and 30% excess reductant was used.

The as-reduced metal product contained typically 1% by weight lanthanum and 1000 ppm by weight oxygen.

When the metal was purified by sublimation at 1100 to 1300°C one sublimation lowered the lanthanum level to 650 ppm and the oxygen to 50 ppm. Two additional sublimations yielded a product containing 20 ppm oxygen and 30 ppm or less lanthanum. A temperature of 1300°C was most desirable since greater sublimation rates were possible with good purification of products.

Dysprosium containing 1000 ppm oxygen was sublimed at

1200, 1300 and 1400°C resulting in products which had only slight differences in oxygen levels.

Dysprosium containing 1% by weight lanthanum was sublimed at 1100°and 1300°C with the 1100°C sublimation giving better lanthanum separation.

When extremely pure dysprosium is desired this method is the most successful to date, but the very high purity is obtained at the expense of high yields.

I. INTRODUCTION

The elements scandium, yttrium, lanthanum and the lanthanide series which includes cerium, atomic number 58, to lutetium, atomic number 71, make up the family of elements referred to as the rare earths (1). The outermost electron configuration of scandium, yttrium and lanthanum metal vapor is that of $(n-1)d\ ns^2$ where n is the principal quantum number. Unlike the transition elements following scandium and yttrium, where electrons are added to the $(n-1)d$ level to complete the series, as electrons are added to yield the lanthanides they are more readily accepted by the inner, well shielded 4f subshell. The resulting lanthanide series plus scandium, yttrium and lanthanum is a group of elements with the same outer electron configuration but having different atomic radii causing them to exhibit differences in those properties which depend upon the radius. As such they are a convenient set of elements for testing theoretical models which relate electronic structure to metallic properties. In the liquid metal the $(n-1)d\ ns^2$ electrons form a conduction band consisting of a sea of electrons which surround ion cores.

There is an increasing demand for very-high-purity, well characterized rare earth metals to be used as specimens in solid-state experimentation. With modern scientific instruments one can make very precise measurements of physical and electronic properties of materials. But since these properties are sensitive to the amount of nonmetallic impurities present one must know the purity of the specimen being measured for these very precise numbers to be of value.

Except for samarium, europium, ytterbium and thulium the most common method for producing rare-earth metals is by calcium reduction of the rare-earth fluorides. Since the fluorides have high boiling points due to low vapor pressures the fluorides don't distill heavily from reaction vessels when heated to reduction temperatures under a vacuum. They also don't build up high pressures if reactions are carried out in sealed bombs.

A major problem with the fluoride method is the complete removal of fluorine from dysprosium metal. Since the volatility of the metal, calcium fluoride and dysprosium fluoride are very similar at a given temperature one cannot completely separate the metal from fluoride impurities. Best techniques during multiple sublimations allow one to obtain fluoride-produced dysprosium metal containing 25 to 75 ppm fluorine.

The problem of fluoride impurities in dysprosium metal can be avoided by using the lithium-rare-earth chloride method where the chloride is reduced with lithium metal (2). The chlorides are however difficult to work with because of their hygroscopic nature and require special dry-box facilities for handling. Furthermore, because of their low boiling points the chlorides have high vapor pressures at reduction temperatures , making it necessary to perform reductions in sealed bombs whose contents are under high pressure.

Because of the high volatility of the chlorides some chloride methods of rare earth metal preparation involve vaporization of the chloride to a gaseous phase followed by reduction of the chloride from the vapor phase.

II. METHODS AND GENERAL CONSIDERATIONS FOR THE DIRECT REDUCTION OF RARE EARTH OXIDES

An alternative method of producing rare earth metals that are not easily prepared in a highly pure state by either the chloride or fluoride method is the direct reduction of the oxide. Direct reduction eliminates the need for an intermediate step wherein the oxide is converted to fluoride or chloride. Except for the reducing agent and oxygen impurities the purity of the final product depends largely on the purity of the reactants. No special handling facilities are needed since rare earth oxides and common reducing agents are relatively stable and can be exposed to air for short lengths of time.

When distillation or sublimation is combined with the oxide reduction the result is a more physically complete separation of product and residue. A necessary requirement for this combination is that the product evolved have a relatively high vapor pressure at the reduction temperature compared to other components within the reaction vessel. As the volatile product forms it will vaporize from the reaction mixture and condense on cool surfaces located outside the heated reaction zone.

The rare earth metals ytterbium, europium, samarium and thulium are well suited for the reduction-distillation process because of their high volatility. Other metals such as dysprosium, holmium and erbium can be produced via this method but are contaminated to a greater extent by the reductant and oxide.

Since the product is continually being removed from the reaction mixture the reduction-distillation process can be driven toward completion even though a reaction is thermodynamically unfavorable under standard conditions. Running the reduction at reduced pressure and at elevated temperature allows the product to vaporize from the reaction mixture and forces the reaction to quantitatively yield the desired product. Using the reduction of dysprosium oxide as a typical example the direct reduction would proceed according to the reaction:

$$1/3Dy_2O_3 + x/yR \rightarrow 1/yR_xO_y + 2/3Dy$$

where R is the reductant.

When one chooses a reductant several factors must be considered. To minimize contamination the reductant should have a relatively low vapor pressure compared to the product at reduction temperatures. Also the reducing agent should not form oxides which would have a volatility comparable to the metal product being collected since this would result in heavy contamination of the product with oxide and reductant.

The melting point of the reductant appears to be important in determining the success of a reduction. Kobisk and Grisham (3) report that reactions employing high-melting reductants such as zirconium and tantalum can be carried out at temperatures well below the reductant's melting point. But under these conditions the yields and rates of product distillation are difficult to control. When lower-melting reductants are used the reaction can be carried out at or above the reducing agent's melting point resulting in smooth reactions with good yields.

III. HISTORICAL

Among the first rare earths to be made by the oxide reduction-distillation method was samarium, which had been difficult to prepare by either the fluoride or chloride process since the dihalide readily formed (4,5). Using this method Spedding _et_ _al_. (6,7) prepared 98% pure metal with yields greater than 80%. Lanthanum was used as the reducing agent. An analysis showed no detectable amounts of lanthanum present in the reduction product.

In addition to samarium the metals ytterbium and europium have been successfully prepared by an identical process (8,9, 10). Yields of greater than 98% have been reported with 300 to 400 grams of metal being prepared at one time.

Lanthanum reduction of the oxide has been extended to the metals erbium, holmium, dysprosium and thulium with varying degrees of success (11). Oxygen contamination was a major problem making it necessary to redistill the metal. Overall yields for reduction and purification were as low as 50% of theoretical for the metals erbium, holmium and dysprosium depending on the extent of oxygen contamination. An equilibrium between the reaction components lanthanum oxide, dysprosium oxide, lanthanum metal and dysprosium metal prevented higher yields from being realized.

Reduction-distillation methods have been used to produce small quantities of rare earth metal isotopes. Westgaard and

Bjornholm (12) reduced ytterbium, samarium and dysprosium oxides with lanthanum (20% in excess of stoichiometric) at temperatures from 1100 to 1750°C realizing yields of 80% in batches which were typically 16 milligrams. The as-reduced metals ytterbium and samarium contained less than 1% lanthanum and the dysprosium contained 5 to 10% lanthanum. Oxides of dysprosium, erbium, neodymium, gadolinium and lutetium were reduced with thorium (100% in excess of stoichiometric) at temperatures from 1650 to 2400°C. Dysprosium, erbium and neodymium distillates contained less than 0.5% thorium while gadolinium and lutetium contained 12% thorium since the vapor pressures of gadolinium and lutetium were more similar to the vapor pressure of thorium than were the vapor pressures of dysprosium, erbium and neodymium. One distillation at temperatures 100 to 200°C below the reduction temperatures lowered the thorium content to less than 1% in gadolinium and 3 to 4% in lutetium. Kobisk and Grisham (13) prepared a number of rare earth isotopes in batches of 20 to 200 milligrams of 99.95% purity (500 ppm total impurity). Collection efficiencies were reportedly 75 to 92% on batches of metal weighing 15 milligrams. Samarium, europium and ytterbium oxides were reduced with lanthanum and praseodymium, promethium, dysprosium, erbium, neodymium and gadolinium oxides were reduced with thorium.

Spedding, Croat and Beaudry (14) reduced 100-gram batches of dysprosium oxide with lanthanum turnings at 1475°C and obtained a product containing about 1% lanthanum and 0.1% by weight oxygen. A similar reduction using zirconium as a reductant was carried out at 1550°C for 100 hours resulting in a 33% yield of product containing less than 1 ppm zirconium and 150 ppm by weight oxygen.

Schiffmacher _et_ _al_. (15,16) reduced dysprosium oxide with thorium (50% in excess of stoichiometric) at several temperatures using a resistance-heated furnace. The dysprosium distillate collected at 1750°C contained 50 ppm thorium and 480 to 550 ppm oxygen. Reductions of dysprosium oxide at several temperatures were also carried out using lanthanum as a reductant (20% in excess of stoichiometric) (17). Electron-bombardment heating was used for these reductions. The dysprosium product obtained from the 1500°C reduction contained 20% lanthanum impurity. One distillation of the product at 1500°C resulted in a product containing 3% lanthanum and a second distillation reduced the lanthanum to 0.2%. Overall yield for the reduction and two distillations was 65%.

IV. PURPOSE

Due to the wide divergence in results of previous direct reduction-distillation studies it was felt the method should be investigated further to resolve these discrepancies. The direct reduction-distillation method is worthy of investigation since it has the potential of producing sizable quantities of ultrapure dysprosium metal. Such a product would be free from the small amount of fluoride impurity commonly present in dysprosium produced using the calcium rare earth fluoride reduction method. Considerable success has been achieved in producing dysprosium metal in milligram quantities by direct reduction leading one to believe that such an operation on a larger scale would also be workable. Success of the method depends largely upon obtaining acceptable yields of products with low reductant and oxide contamination in the as-reduced state which can be later purified with a minimum amount of sublimation.

The amount of excess lanthanum reductant needed to give greatest product yields and the conditions necessary to obtain the highest metal purity will be investigated in this work. Also the profile of product contamination by reductant and oxide as a function of yield is needed to determine a practical reduction time.

Since sublimation is used to purify the as-reduced metal information about the effect of sublimation rate on the removal of lanthanum reductant and oxide is needed to get maximum metal purification in a reasonable period of time.

Information related to the direct reduction-distillation technique had been collected during the preparation of high purity dysprosium metal for physical property measurements in this laboratory. When this information was gathered only final product purities and yields were of importance so a number of critical analyses were not made. However, such information was valuable in evaluating the process and for that reason it was included in this study.

V. EQUIPMENT

A. Resistance Furnace Used in Reductions and Sublimations

A number of reductions and all sublimations were carried out in a tantalum-tube resistance furnace which is illustrated in Fig. 1. The stainless steel vacuum chamber, measuring 6" in diameter by 18" long, was of double-wall construction with water circulating between the walls for cooling purposes.

The 2.5" diameter resistance heater had an 8" heat zone constructed of .002" tantalum. Heavier end sections were spot-welded to the .002" heater material to provide rigidity and as a means for connecting the heating column to copper electrodes. Because the end sections were constructed of .005" and .010" tantalum they would remain relatively cool while passing a current that produced 1650°C in the heat zone. Tabs were cut and bent in the end sections and copper rings with screws were used to fasten the column to the electrodes.

Six concentric radiation shields were positioned between the heater and water jacket. All shields were of .010" tantalum except the outermost, which was of .015" molybdenum. The molybdenum shield was used only because of convenience as it had been constructed for an earlier furnace design.

Thermocouples entered the system through a Conac gland in the furnace base. Pt-Pt13%Rh thermocouples surrounded by high purity Al_2O_3 insulators were used to measure the temperature in all reductions and sublimations except the 1750°C reduction.

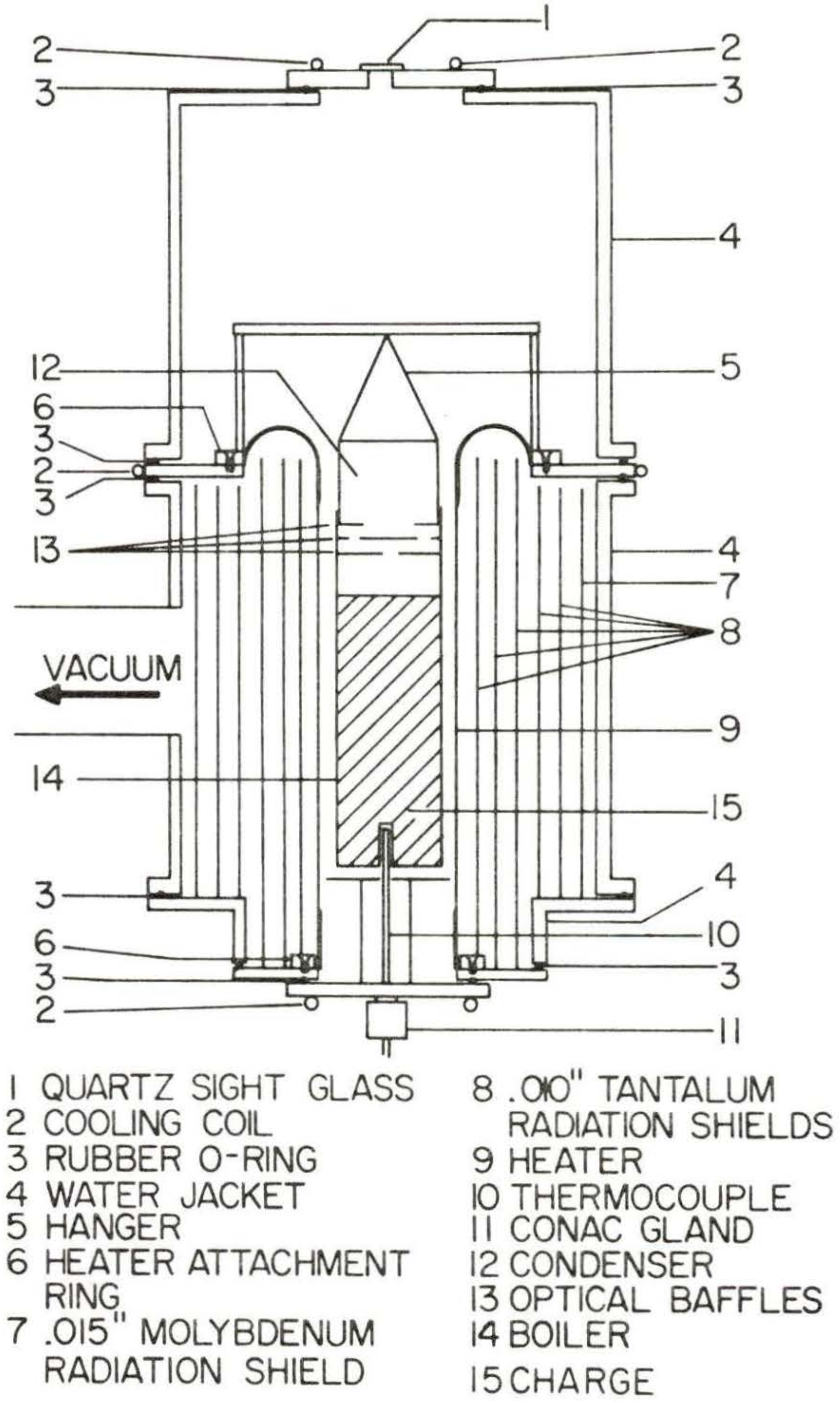

Fig. 1. Resistance furnace

During the 1750°C reduction W5%Re-W26%Re thermocouples were used.

To provide protection from metal vapors and support at high temperatures a sheath of .156" diameter tantalum tubing, sealed at one end, was placed over the thermocouple and insulator. Because the platinum thermocouple bead and tantalum sheath interacted at operating temperatures, giving erroneous readings, it was necessary to surround the bead with a protecting insulator. This was done by drilling a hole large enough to accommodate the bead in the end of the insulator carrying the wires. The bead was recessed in the insulator and capped with another .25" length of insulator before the tantalum sheath was slipped over the thermocouple.

Thermocouple EMF's were measured with a Leeds and Northrup K-4 potentiometer.

The vacuum system was a Welch Duoseal #1397 mechanical fore pump and a 5" NRC oil diffusion pump connected in series. Free air displacement of the fore pump was 425 liters/minute. Pumping speed of the diffusion pump was 750 liters/second for air and Dow 702 silicon oil was the pumping fluid.

A set of baffles, cooled by a refrigeration unit, was situated between the diffusion pump and furnace. The baffles reduced backstreaming of oil into the heating chamber by obstructing the pathway and providing a surface upon which oil vapors could condense.

Pressures were measured with a cold-cathode ionization gauge positioned between the diffusion pump inlet and the heating chamber. The pumping system was capable of producing a vacuum of 1×10^{-7} torr after the system had been allowed to outgas for several hours.

Furnace power was supplied by a double-ganged, adjustable powerstat and step-down transformer. A current of approximately 25 amperes was required to attain a temperature of 1650°C.

B. Furnace Using Induction Heating

A vacuum furnace employing induction heating was used for two reductions. As illustrated in Fig. 2 the vacuum chamber consisted of a 5.50" diameter by 24" long fused quartz tube around which was an induction coil.

Inside the quartz tube was a 3.50" diameter by 10" long heater constructed from .030" tantalum within which the reduction vessel was placed. Graphite felt insulation surrounding the heater held the heater in place.

The vacuum system consisted of a Welch Duoseal #1397 mechanical fore pump and a Consolidated Electrodynamics Corporation MCF-300 oil diffusion pump equipped with a liquid nitrogen cold trap. The pumping medium for the diffusion pump was Dow 702 silicon oil.

The furnace was heated by a water-cooled induction coil which was 6" in diameter by 10" long. The coil was wound with four turns per inch of height.

Power was supplied to the coil by an Ajax-Northrup, 20

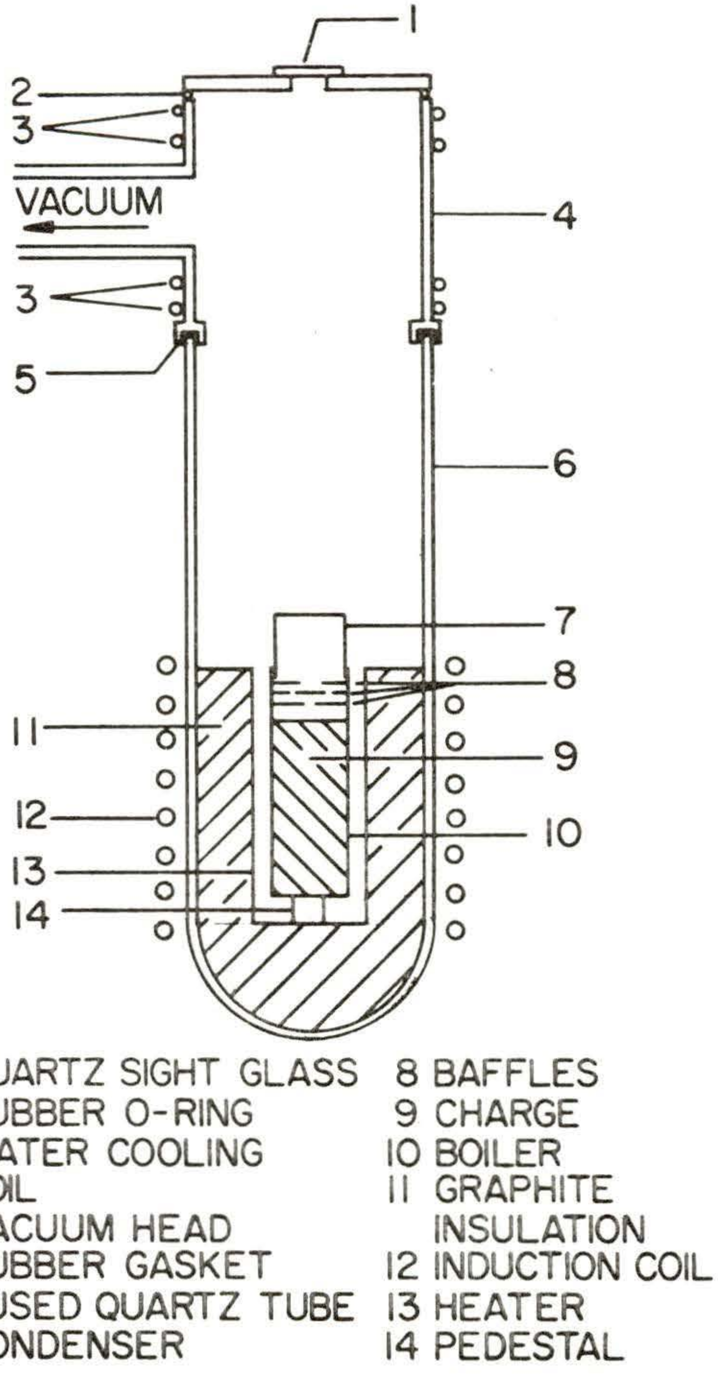

Fig. 2. Induction heated furnace

kilowatt high frequency (20,000 cycles/second) converter.

C. Arcmelter

An arcmelter, constructed at the Ames Laboratory, was used to homogenize metal products obtained from reductions and sublimations and to prepare the alloys used in sublimation studies. Samples were melted on a water-cooled copper hearth by a nonconsummable, tungsten electrode under an atmosphere of pure argon. Prior to melting samples a zirconium button was held molten for 1 to 2 minutes to getter any reactive gases present. A Welch Duoseal #1397 mechanical fore pump was used to evacuate the system. The arcmelter is illustrated in Fig. 3.

D. Tantalum Condensers, Boilers and Baffles

Experience of workers engaged in rare earth metal preparation has shown tantalum is a superior material from which to fabricate reaction vessels. Ease of welding, high melting point, ductility and high degree of resistance to chemical attack are a few of its desirable characteristics. Because of its high melting point tantalum is soluble only to a small extent in most low-melting, rare-earth metals. Removal is accomplished by holding molten rare earth metals five to ten degrees above their melting points and allowing second-phase tantalum to settle to the bottom of the melt. For the rare earth metals having high melting points sublimation is quite successful in removing tantalum.

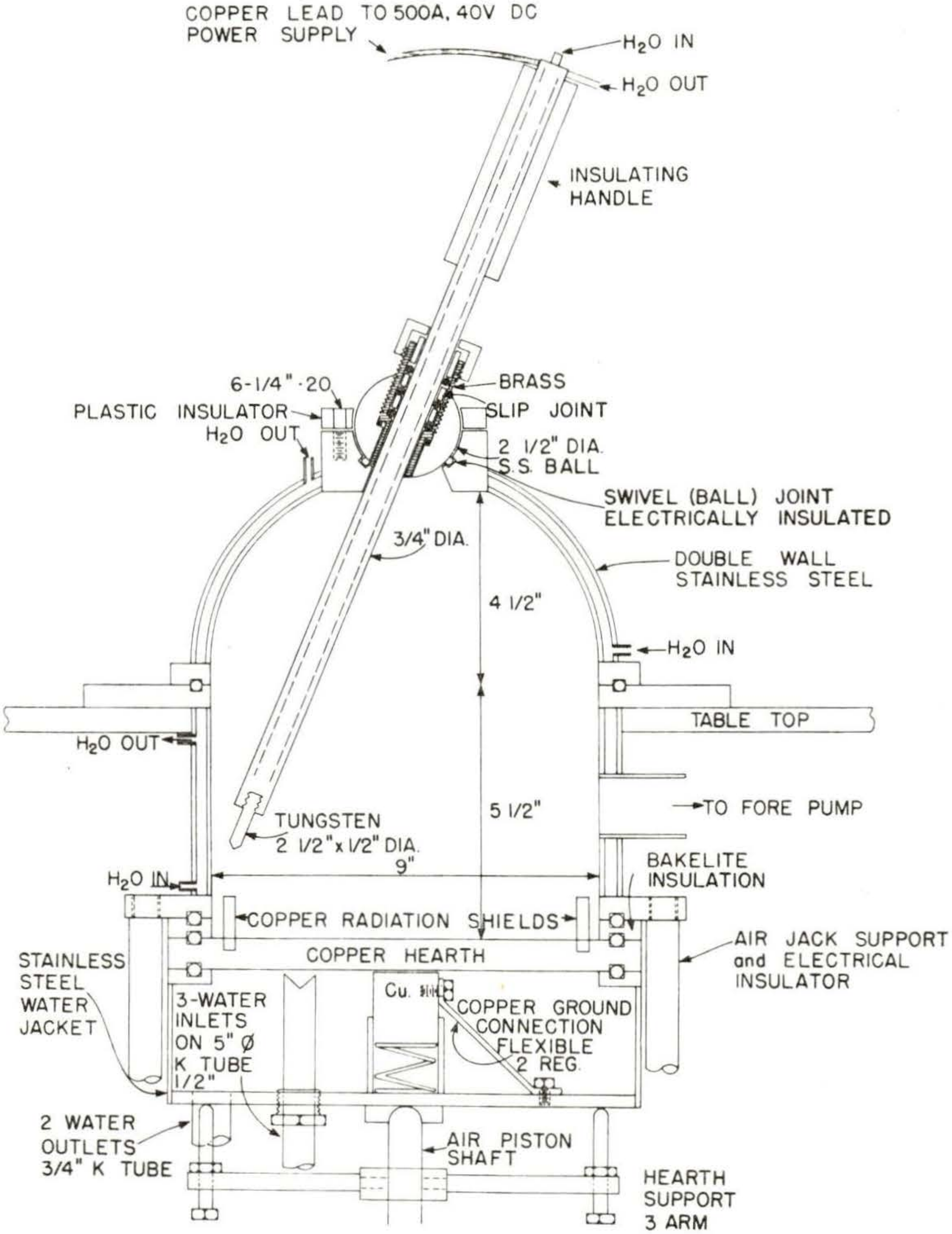

Fig. 3 Arcmelter

Boilers and condensers of two different diameters were used throughout this study. All reductions and sublimations employing the resistance-heated vacuum furnace, which was described in Section V. A. and illustrated in Fig. 1, were 1.625" diameter vessels. The reductions carried out in the induction heated furnace, described in Section V. B. and illustrated in Fig. 2, had a diameter of 2.5".

All condensers were fabricated from .005" thick tantalum stock. Tops were drawn on a two piece die and spotwelded to the condenser sides. The length of condenser used with small (1.625" dia.) reaction vessels was 1.5" for both reductions and sublimations. Large (2.5" dia.) reaction vessels used condensers 2.3" long.

Boilers were constructed of .030" thick tantalum. In the case of the small (1.625" dia.) vessels boilers were 6" in length when used in reductions and 5" in length when used in sublimations. Large (2.5" dia.) reduction boilers were 9.25" long.

After each boiler was cold rolled to the proper diameter the resulting seam and bottom were welded in a helium filled welder similar to that described by Miller et al. (18).

When the temperature was determined by a thermocouple rather than an optical pyrometer, which was used for the higher temperatures in early experiments, a 0.25" diameter by 1.5" long well was welded to each boiler bottom. The use of such a well gave a more representative temperature of the vessel's contents than did a thermocouple positioned along the outer walls of the boiler.

To prevent leakage of the product while reductions and sublimations were in progress it was necessary to have a good mechanical fit where the condenser joined the boiler. This was achieved by expanding the upper lip of the boiler with a tapered shaft. A condenser constructed with the proper diameter could be pressed approximately .125" into the boiler with a resulting joint through which only slight amounts of metal were lost.

Line of sight baffles were used in the reduction boilers to reduce entrainment of impurities as the product evolved. The baffles also served as radiation shields between the condenser and boiler. Three baffles, constructed of .010" tantalum, were placed near the boiler tops to eliminate the direct path between product and reactants.

Orifice areas of the three baffles were related to the vapor pressure of dysprosium metal. By determining the temperature of each baffle a vapor pressure could be calculated using the equation developed by Habermann and Daane (19):

$$\log P_{mm} = 8.822 \pm .035 - \frac{(15,090 \pm 52)}{T}$$

where P is the pressure in millimeters of mercury and T is temperature in degrees Kelvin. The relationship between baffle orifice areas was chosen to be approximately inversely proportional to the relationship between calculated vapor pressures of dysprosium metal at the baffle temperatures.

Baffle temperatures were determined by heating an empty 1.625" diameter condenser-boiler assembly to 1650°C in the resistance furnace and making measurements with a Leeds and Northrup Model 8622-C optical pyrometer. Temperatures were 1215, 1335 and 1455°C for the upper, middle and lower baffles respectively. Table 1 gives a summary of the number and size of orifices used in the reduction vessels.

Table 1. Orifices used in reduction vessel baffles.

Baffle	1.625" dia. vessel		2.5" dia. vessel	
	Number of orifices	Orifice diameters	Number of orifices	Orifice diameters
Upper	1	.75"	1	1.15"
Middle	4	.25"	4	.33"
Lower	1	.25"	1	.33"

Baffle spacing for the 1.625" diameter vessels was .25" with the uppermost baffle being .5" from the boiler top. Baffles in the 2.5" diameter vessels had a spacing of .375" with the top baffle being .75" below the boiler top.

Before use, all condensers, boilers and baffles were outgassed at 2000°C for one hour or until the pressure in the outgassing furnace dropped to 2-3 x 10^{-5} torr.

VI. MATERIALS

A. Lanthanum

Lanthanum used in this study was prepared using the fluoride method as described by Spedding et al. (20). Lanthanum fluoride was prepared using the method of Spedding and Henderson (21) by heating the oxide in a platinum boat to 750°C for 10 hours in the presence of HF gas. The fluoride was reduced with high purity calcium under an argon atmosphere at 1450°C. After removing the CaF_2 slag the lanthanum metal was vacuum-melted at 1800°C to remove volatile impurities. Three 1-kilogram batches of metal were prepared for use as a reductant and as a dopant in sublimation studies. A typical analysis of the resulting products as determined by mass spectrometry is shown in Table 2.

Lanthanum was used as turnings in the reduction of dysprosium oxide. Turnings were made in air since heavy oxygen contamination from the dysprosium oxide reactant was inevitable. Chips were machined using a lathe with the lanthanum workpiece rotating at a low rpm. To insure uniform particle size a cut of .050" was always taken. Approximately twenty minutes was required to machine 110 grams of turnings.

B. Dysprosium Oxide

The dysprosium oxide was obtained from Dr. Powell's Physical and Inorganic Chemistry Group. An ion-exchange method as described by Powell and Spedding (22) had been used to sep-

Table 2. Typical analysis of lanthanum metal used as a reductant. Values are in parts per million atomic.

Impurity		Impurity	
H	2100(13)[a]	Pr	14
N	15(1.3)	Nd	4
O	240(24)	Sm	.5
F	2	Eu	1
Mn	.2	Gd	2
Fe	350	Tb	8
Ni	50	Dy	3
Cu	1	Ho	.1
Zn	.6	Er	.4
Ta	35	Tm	.1
W	3	Yb	.5
Y	.7	Lu	1
Ce	10		

[a] Values are in parts per million by weight.

arate and purify the oxide.

Before use the oxide was placed in a platinum boat and heated to 850°C for 24 hours in a muffle furnace to drive off any water that might be present. An analysis of the oxide as determined by mass spectrometry is shown in Table 3.

Table 3. Typical analysis of dysprosium oxide used in reductions. Values are in parts per million atomic.

Impurity		Impurity	
Cl	70	Ce	.8
Ca	85	Pr	2.5
Cr	5	Nd	.4
Mn	10	Sm	.3
Fe	16	Eu	1
Ni	1	Gd	2
Cu	.6	Tb	6
Zn	6	Ho	3
Pb	6	Er	1
Sc	5	Tm	2
Y	7	Yb	1.1
La	2	Lu	11

VII. EXPERIMENTAL PROCEDURES AND RESULTS

A. Reduction of Oxide

1. Reductions in the resistance furnace

Four reductions were carried out in the tantalum-tube resistance furnace described in Section V. A. and illustrated in Fig. 1. Dysprosium oxide, which had been heated to 850°C for 24 hours, and freshly-machined lanthanum chips were mixed in a plastic bag. The amount of lanthanum reductant used was 20% in excess of that required to stoichiometrically reduce the oxide. As the mixture was transferred to the 1.625" diameter tantalum boiler it was frequently tamped with a steel shaft to provide good oxide to chip contact. The three line-of-sight baffles were then driven into place with a steel shaft. After placing the condenser atop the boiler the reduction assembly was positioned in the resistance furnace so that the upper lip of the boiler was at the same level as the top of the 8" heat zone.

When the furnace had been evacuated to 1×10^{-6} torr the mixture was heated to 800 to 910°C for 12 hours. Because the mixture outgassed heavily it was necessary to increase the power slowly to keep the pressure in the 10^{-5} torr range, but at the end of the 12-hour period the pressure was normally in the low 10^{-6} torr range.

During the 12-hour period the lanthanum chip surface reacted with oxide preventing molten lanthanum from flowing to the bottom of the boiler when the temperature was later increased.

As the mixture was heated to 1650°C for the actual reduction moderate outgassing occurred. Pressure was maintained in the 10^{-5} torr range during heating but it dropped to the mid 10^{-7} torr range after the temperature had been at 1650°C for several hours.

Temperatures for the four reductions were measured with a Leeds and Northrup Model 8622-C optical pyrometer.

At the end of the reduction period the porous, grey-black residue remaining in the boiler was dissolved in hot hydrochloric acid. Several hours of boiling in acid were necessary to dissolve all of the material. After rinsing with distilled water and acetone the boiler was outgassed and reused.

Condensers were removed from the reduction product by machining on a lathe.

The products, weighing 125 to 150 grams each were homogenized in the argon-filled arc melter by melting four times, turning the bar after each melt. The results of the four reductions are summarized in Table 4.

2. Reductions to determine effect of excess lanthanum

Five reductions were run at 1650°C in which the amount of lanthanum reductant used was stoichiometric, 5%, 10%, 20% and 30% in excess of stoichiometric. Each reduction was carried out in the tantalum-tube resistance furnace described in Sec-

Table 4. Summary of yields and analyses for four reductions in the resistance furnace. Values are in parts per million atomic unless otherwise indicated.

Reduction	Time at 1650°C	Weight of product	Yield	La	O	H	N
1	75 hrs	155 g	81%	1%	1740	5	8
2	67 hrs	135 g	71%	1%	974	7	1
3	72 hrs	125 g	56%	1%	1045	3	3
4	98 hrs	135 g	77%	—[a]	—[a]	—[a]	—[a]

[a] Value not determined.

tion V. A. and illustrated in Fig. 1. The procedure used in charging the boiler with reactants and heating the charge was identical to that described in Section VII. A. 1. The reduction was stopped after being at 1650°C for a total of 2, 5, 9, 15 and 25 hours. During each of the interruptions the condenser and product which had accumulated was replaced with a fresh condenser. After each fraction of product was collected the boiler was weighed to determine weight changes and hence the amount of material sublimed.

Pt-Pt13%Rh thermocouples were used to determine temperatures. Because the thermocouples deteriorated rapidly at 1650°C due to a reaction with the insulator material, it was necessary to pull fresh wire into the hot zone and weld a new bead after each fraction of product had been collected.

By carefully adjusting the powerstat it was possible to maintain the temperature within ±5° of that desired.

Condensers were machined away from the product on a lathe.

Each fraction of product was homogenized in the argon-filled arcmelter by melting four times, turning after each melt. Results of the weights and sublimation rates of products collected are shown in Table 5. Analyses of these products are shown in Table 6. The results of Table 5 are plotted in Fig. 4.

3. Reduction of dysprosium oxide at 1750°C

A reduction of dysprosium oxide by lanthanum was carried out at 1750°C in the tantalum-tube resistance furnace described in Section V. A. and illustrated in Fig. 1. A 10% stoichiometric excess of lanthanum was used. The method used in charging the boiler, heating the reactants and interrupting the reduction at 2, 5, 9, 15 and 25 hours was identical to the procedure described in Section VII. A. 2. After carrying out the reduction for the usual 25 hours the reaction mixture was heated an additional 10 hours with a 2.0" condenser instead of the usual 1.5" condenser.

As stated earlier W5%Re-W26%Re thermocouples were used because of their greater resistance to deterioration at high temperatures.

Analyses were made from each fraction after it had been homogenized by melting four times in the argon-filled arc melter.

Unlike the 1650°C reduction residues which were porous, grey-black clinkers, the residue from the 1750°C run was a solidified mass which appeared to have been entirely molten

Table 5. Summary of product weights, sublimation rates and yields for five reductions at 1650°C using different amounts of lanthanum reductant.

Total time at 1650°C	Amount of lanthanum reductant used				
	Stoichio-metric	5% excess lanthanum	10% excess lanthanum	20% excess lanthanum	30% excess lanthanum
	818°C[a]	816°C	775°C	815°C	798°C
2 hr	(40.9 g)[b] 20.4 g/hr[c]	(38.8 g) 19.4 g/hr	(39.5 g) 19.8 g/hr	(37.6 g) 18.8 g/hr	(34.7 g) 17.4 g/hr
5 hr	(21.1 g) 7.0 g/hr	(21.3 g) 7.1 g/hr	(22.5 g) 7.5 g/hr	(20.4 g) 6.8 g/hr	(19.5 g) 6.5 g/hr
9 hr	(11.8 g) 2.9 g/hr	(13.4 g) 3.4 g/hr	(14.0 g) 3.5 g/hr	(14.6 g) 3.6 g/hr	(14.8 g) 3.7 g/hr
15 hr	(7.1 g) 1.2 g/hr	(9.8 g) 1.6 g/hr	(8.9 g) 1.5 g/hr	(9.8 g) 1.6 g/hr	(11.7 g) 1.9 g/hr
25 hr	(5.7 g) .57g/hr	—[d] —[d]	(6.3 g) .63g/hr	(8.0 g) .80g/hr	(8.7 g) .87g/hr
Overall yield	69.4%	—[d]	73.0%	72.3%	71.5%

[a] Temperature at which charge was held for 12 hours prior to actual reduction.

[b] Weight of fraction collected.

[c] Sublimation rate for fraction collected.

[d] Boiler developed leak.

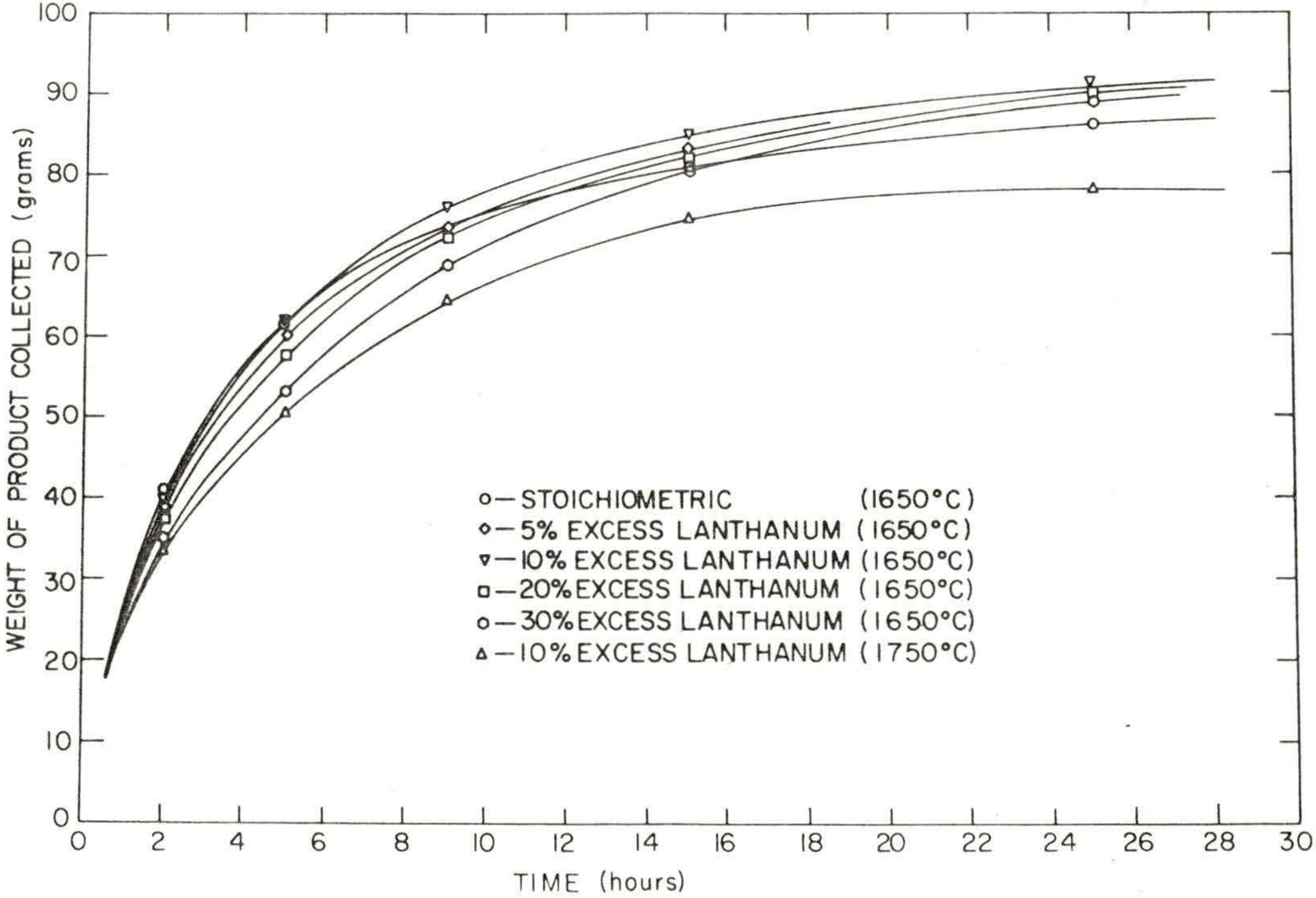

Fig. 4. Plot of product collected versus time for different excesses of lanthanum reductant

Table 6. Analysis of products collected from five reductions in which the amount of lanthanum reductant was varied. Values for lanthanum are in percent by weight. All other values are in parts per million by weight.

Total time at 1650°C	Impurity	Amount of lanthanum reductant used				
		Stoichiometric	5% excess lanthanum	10% excess lanthanum	20% excess lanthanum	30% excess lanthanum
2 hrs	La	.43	.35	.50	.45	.80
	O	150	220	97	101	142
	H	7	7	5	5	6
	N	30	13	4	6	4
5 hrs	La	1.40	2.10	2.00	1.20	2.40
	O	213	192	196	176	292
	H	3	5	5	4	7
	N	34	54	8	14	24
9 hrs	La	1.00	.94	1.45	2.10	3.50
	O	695	420	445	409	458
	H	16	9	8	6	7
	N	56	94	8	44	29
15 hrs	La	3.00	1.10	1.40	1.20	2.00
	O	1271	771	906	778	729
	H	4	9	11	9	8
	N	143	59	11	92	52
25 hrs	La	4.70	2.30	2.20	3.50	4.50
	O	2528	1613	1581	1829	1963
	H	21	12	7	25	12
	N	265	71	11	139	64

at the reduction temperature.

A summary of the product weights and sublimation rates as well as analytical results are presented in Table 7. A plot of product weight versus time is shown in Fig. 4.

Table 7. Summary of the 1750°C reduction of dysprosium oxide using a 10% excess of lanthanum reductant. Lanthanum values are in percent by weight. All other values are in parts per million by weight.

Total time at 1750°C	Product collected	Dysprosium collected	Impurity			
			La	O	H	N
2 hrs	(33.3 g) 16.6 g/hr[a]	32.7 g	1.90	252	5	27
5 hrs	(17.2 g) 5.7 g/hr	17.0 g	1.10	656	10	65
9 hrs	(14.0 g) 3.5 g/hr	13.0 g	2.20	645	10	2
15 hrs	(10.2 g) 1.7 g/hr	9.9 g	3.10	2136	10	115
25 hrs	(3.9 g) .39g/hr	3.1 g	21.0	—[b]	—[b]	—[b]
35 hrs	(5.9 g) .59g/hr	2.4 g	60.0	—[b]	—[b]	—[b]
Overall yield	67.6%	62.5%				

[a] Sublimation rate for fraction collected.

[b] Insufficient amount of product collected for complete analysis.

4. Reductions in the induction furnace

Two reductions were carried out in a vacuum furnace heated by induction which was described in Section V. B. and illustrated in Fig. 2.

Each charge was loaded into the 2.5" diameter boiler with frequent tamping. After the three baffles and condenser were installed the reduction column was placed in the furnace so that the boiler's upper lip was at the same level as the top of the tantalum heater as illustrated in Fig. 2.

The furnace was evacuated to 1 x 10^{-6} torr and the charge heated for 2 hours at 800°C. Following the 2-hour heating period the actual reduction was begun by slowly heating the column to the desired temperature. Temperature determinations were made with a Leeds and Northrup Model 8622-C optical pyrometer.

The two reductions are summarized in Table 8.

Table 8. Reduction-distillations carried out in the induction heated vacuum furnace.

Reduction	Charge		Prereduction heating	Reduction time and temperature	Yield
	Dy_2O_3	La			
1	400 g	393 g[a]	2 hours at 800°C	4 hours at 1650°C	78.5%
2	693 g	567 g[b]	2 hours at 800°C	21 hours at 1575 to 1600°C	64.4%

[a] A 32% excess of reductant.

[b] A 10% excess of reductant.

B. Purification of Metals

All purification operations were carried out in the resistance furnace described in Section V. A. using 1.625" diameter reaction vessels.

All sublimation boilers described in this section were equipped with .25" diameter by 1.5" long thermocouple wells into which Pt-Pt13%Rh thermocouples were placed. Thermocouple EMF's were measured on a Leeds and Northrup K-4 potentiometer.

1. Sublimation of reduction products

The first three reduction products in Section VII. A. 1. (a total of 300 grams) were melted into a homogeneous bar in the argon-filled apparatus described in Section V. C. The as-reduced metal contained approximately 1% by weight lanthanum. After cutting the bar into smaller pieces which would easily fit into the sublimation column the metal was sublimed at 1200, 1125 and 1100°C in that order. Following each sublimation the condensers were machined from the products and the products homogenized in the arc melter by melting four times, turning the bar after each melt. A partial analysis was made after the first and third sublimation. Table 9 is a summary of the three sublimations.

Table 9. Summary of three sublimations of reduction products. Values are in parts per million by weight.

Sublimation	Temperature	Sublimation rate	Impurities			
			La	O	H	N
1	1200°C	8.9 g/hr	641	58	2.6	31
2	1125°C	2.5 g/hr	—[a]	—[a]	—[a]	—[a]
3	1100°C	1.0 g/hr	9	21	1.8	24

[a] Value not determined.

The product resulting from the second reduction in the induction-heated furnace (Section VII. A. 4.) containing approximately 1% by weight lanthanum was sublimed three times at temperatures of 1100, 1098 and 1095°C in that order. After each sublimation condensers were machined from products, the products homogenized in the arc melter by melting four times under an atmosphere of argon and an analysis of the ingots completed. Table 10 is a summary of the analyses made of the reduction products.

2. Sublimation of dysprosium containing oxygen at 1200, 1300 and 1400°C

Dysprosium-oxygen alloys were sublimed at 1200, 1300 and 1400°C to determine the effect sublimation rates have on the removal of oxygen.

Three alloy bars were prepared in an arc melter by dissolving a known amount of dysprosium oxide powder in molten dysprosium metal. Enough oxide was used to give an alloy containing approximately 1000 ppm by weight oxygen, which is about the same level of oxygen impurity present in as-reduced dysprosium prepared by the lanthanum reduction of oxide. Analyses of the alloys before sublimation are presented in Table 11.

The product of each sublimation was collected in five fractions. Condensers were machined from each fraction of product and the product homogenized for analysis in the arc melter. Table 12 summarizes the three sublimations.

Table 10. Analysis of three sublimations of dysprosium produced in the induction heated furnace. Values are in parts per million atomic except where noted.
(1) First sublimation at 1100°C.
(2) Second sublimation at 1098°C.
(3) Third sublimation at 1095°C.

Impurity	(1)	(2)	(3)	Impurity	(1)	(2)	(3)
H	322(2)[a]	483(3)	644(4)	Ce	.3	.2	.2
N	140(12)	47(1)	47(1)	Pr	.2	.1	.05
O	306(30)	163(16)	102(10)	Nd	.6	2	1
F	—[b]	10	10	Sm	.3	.1	.2
Fe	15	10	50	Eu	.2	.2	.1
Ni	.2	.1	.4	Gd	.5	.2	.6
Cu	5	20	60	Tb	1	1	.7
Zn	.1	.01	.1	Ho	3	2	2
Ta	100	5	.8	Er	2	.8	1
W	1	1	.5	Tm	5	1	.2
Y	.6	.3	.3	Yb	.5	2	.5
La	670	60	30	Lu	1	.8	.4

[a] Values in parentheses are in parts per million by weight.

[b] Value not determined.

Table 11. Analysis of dysprosium-oxygen alloys before sublimation at 1200, 1300 and 1400°C. Values are in parts per million by weight.

Sublimation Temperature	Impurities		
	Oxygen	Hydrogen	Nitrogen
1200°C	1049	8	30
1300°C	——[a]	——[a]	——[a]
1400°C	910	6	12

[a] Value not determined but assumed to be similar to the alloys sublimed at 1200 and 1400°C.

3. Sublimation of dysprosium containing lanthanum at 1100 and 1300°C

Dysprosium containing approximately 1% lanthanum by weight was sublimed at 1100 and 1300°C to determine the effect of sublimation rate on the removal of lanthanum. Two dysprosium-lanthanum alloys were prepared by melting the parent metals in the arc melter. The first alloy was sublimed at 1100°C and the second at 1300°C, with the product of each sublimation being collected in five fractions. Condensers were machined from the products and the products homogenized by melting four times before analysis. The two sublimations are summarized in Table 13.

Table 12. Results of 1200°C, 1300°C and 1400°C sublimations of dysprosium containing oxygen. Values are in parts per million by weight.

Temperature of sublimation	Fraction	Weight collected	Percent collected	Sublimation rate for run	Analysis of fractions		
					O	H	N
1200°C	1	11.5 g	6.4 %	11.5 g/hr	56	10	9
1200°C	2	28.5 g	15.8 %	8.2 g/hr	54	4	12
1200°C	3	86.0 g	47.8 %	7.9 g/hr	30	3	12
1200°C	4	38.0 g	21.0 %	6.9 g/hr	35	5	9
1200°C	5	12.0 g	6.6 %	4.5 g/hr	70	10	15
		3.0 g[a]	1.7 %[a]				
1300°C	1	16.0 g	9.1 %	32.0 g/hr	71	5	14
1300°C	2	41.5 g	23.7 %	35.6 g/hr	52	2	2
1300°C	3	65.0 g	37.1 %	37.1 g/hr	52	2	1
1300°C	4	36.0 g	20.6 %	34.3 g/hr	79	4	7
1300°C	5	10.0 g	5.7 %	20.8 g/hr	120	7	13
		4.5 g[a]	2.6 %[a]				
1400°C	1	18.9 g	9.0 %	113.5 g/hr	77	5	12
1400°C	2	46.3 g	22.0 %	138.8 g/hr	36	1	6
1400°C	3	71.1 g	33.8 %	115.0 g/hr	45	1	4
1400°C	4	37.6 g	17.8 %	107.0 g/hr	53	N.D.	4
1400°C	5	24.6 g	11.6 %	73.6 g/hr	123	4	5
		11.3 g[a]	5.4 %[a]		6253[a]	21[a]	106[a]

[a] Residue remaining in boiler.

Table 13. Results of sublimations of dysprosium containg lanthanum at 1100°C and 1300°C. All values are in parts per million by weight.

Temperature of sublimation	Fraction	Weight collected	Percent collected	Sublimation rate for run	Analysis of fractions La	O	H	N
1100°C	1	20.0 g	17.4 %	1.74 g/hr	446	72	6	13
1100°C	2	15.6 g	13.0 %	1.30 g/hr	42	86	6	11
1100°C	3	56.6 g	47.2 %	1.18 g/hr	10.2	54	4	2
1100°C	4	15.1 g	12.6 %	.92 g/hr	6.4	76	5	8
1100°C	5	10.0 g	8.3 %	.65 g/hr	19.7	100	4	9
		1.9 g	1.6 %					
1300°C	1	21.8 g	15.2 %	50.4 g/hr	68.5	62	7	12
1300°C	2	24.1 g	16.8 %	55.6 g/hr	23.1	115	13	13
1300°C	3	44.8 g	31.1 %	44.8 g/hr	12	58	4	3
1300°C	4	17.3 g	12.0 %	40.0 g/hr	12	64	5	8
1300°C	5	28.7 g	19.9 %	33.8 g/hr	19.7	41	4	11
		7.2 g	5.0 %					

VIII. DISCUSSION AND CONCLUSIONS

Dysprosium metal can be prepared in high purity except for fluorine by the calcium reduction of dysprosium fluoride. However for some very precise experimental measurements it is desirable to use specimens with very low fluorine so a procedure other than the fluoride method must be used. The thermal reduction of oxide by lanthanum has proved successful for the more volatile rare earths ytterbium, europium, samarium and thulium and early experiments using this method had shown promise for producing dysprosium metal in high purity form. This study has shown that sizable quantities of dysprosium metal can be prepared in high purity by the lanthanum reduction of oxide.

The direct reduction of oxide involves fewer steps than either the calcium reduction of the rare earth chloride or fluoride. The oxide is reduced directly eliminating the halide intermediate. Not only does this shorten the process but also reduces the chance for impurities entering the product.

A major disadvantage of the direct reduction method as performed in this study was the low yields realized. Yields were typically in the neighborhood of 70 to 75% of theoretical when reductions were run at 1650°C, which is well below the yields attained when using the chloride or fluoride methods.

Approximately the first 50% of the reduction product was collected at a good distillation rate but as one continues the reaction the rate of collection diminishes considerably as 70 to 75% yield is approached. Also the product collected as the maximum yield is approached contained appreciable amounts of reductant and oxide impurities.

The yield did not improve when the reaction was run at a higher temperature. A reduction was run at 1750°C using a 10% stoichiometric excess of lanthanum resulting in a yield of 62.1% after 25 hours. This was increased to 67.6% by running for an additional 10 hours with a 2" condenser.

Results of this study show the yield is rather insensitive to the amount of excess reductant used, with less than 5% separating the highest and lowest yields as the amount of reductant is varied from stoichiometric to 30% in excess of stoichiometric. The best yield at 1650°C was obtained by using an amount of lanthanum which was 10% greater than stoichiometrically required to reduce the oxide.

Lanthanum content of the reduction product increases considerably as the reaction proceeds toward completion. The fraction collected during the first two hours at 1650°C, representing approximately 30% of the theoretical yield, contained typically 0.5% by weight lanthanum. The final portion of product collected during a ten-hour period at 1650°C contained several weight percent lanthanum and made up about 5% of the theoretical yield. By running the reduction for a shorter length of time one could obtain a purer product with only a small reduction in the overall yield.

The lanthanum impurity in similar fractions of reductions using different excesses of lanthanum reductant remains approximately the same as the amount of excess reductant is varied from stoichiometric to 30% in excess of stoichiometric. When all of the fractions from a single reduction are melted together the resulting ingot contains about 1% by weight lanthanum in the as-reduced state.

The oxygen impurity of the dysprosium condensate from the reduction also increases significantly as the reduction progresses. Initial fractions contain typically 100 to 200 ppm by weight oxygen while final fractions contain 1500 to 2500 ppm by weight. As in the case of lanthanum contamination, shorter reduction times would produce a purer product without significantly reducing the yield. When all fractions of a single reduction are melted together the result is an ingot having 1000 ppm oxygen.

The impurities nitrogen, and to a lesser extent hydrogen, increase as the reduction proceeds but are present at much lower levels than either lanthanum or oxygen.

In the lanthanum reduction of dysprosium oxide carried out at 1750°C the first several fractions of product collected had lanthanum impurities slightly higher than the 1650°C reductions. But the last two fractions collected at 1750°C had much higher lanthanum levels than did similar fractions in the lower temperature reductions. Oxygen impurity in the 1750°C reduction products was much higher than in the 1650°C products but the impurities hydrogen and nitrogen remained at levels similar to the lower-temperature reduction products.

The as-reduced product was successfully purified with respect to both lanthanum and oxygen by sublimation. When the as-reduced dysprosium product, which commonly contained 1% by weight lanthanum, was sublimed at 1100 or 1200°C a 15-fold reduction in lanthanum content was realized. Further purification was realized when products were sublimed twice at about 1100°C. The triply-sublimed products contained 9 ppm by weight lanthanum in one case and 30 ppm in another. There appeared to be little difference in the extent of lanthanum removal from dysprosium-1% lanthanum alloys at 1100°C and 1300°C. Lanthanum content was higher in the initial fraction collected at 1100°C than the initial 1300°C fraction.

When dysprosium metal containing about 1000 ppm oxygen was sublimed once at 1200°C a product resulted which had around 50 ppm oxygen. Additional sublimations at 1100°C lowered the oxygen content to a level of about 20 ppm below which it was difficult to achieve further purification. The degree to which oxygen was removed from dysprosium does not differ greatly if the sublimation was carried out at 1200 or 1400°C. The sublimation rate was much greater at the higher temperature allowing one to perform more than one sublimation and obtain a purer product than could have been achieved in a single, low-temperature sublimation taking the same amount of time.

It has been demonstrated that dysprosium metal can be produced by the direct reduction of dysprosium oxide with lanthanum. Sublimation was necessary to obtain a very pure product almost free of lanthanum and gaseous impurities. The fluorine content of the metal was lower than in dysprosium obtained using the fluoride method. However the pure dysprosium metal was obtained at the expense of good overall yields. Both the lithium-rare-earth-chloride and calcium-rare-earth-fluoride reduction methods give much better yields of dysprosium metal. It was concluded that use of this method on a larger scale to produce dysprosium metal relatively free of fluorine should include a process for recovery of the dysprosium remaining in the reduction slag.

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