EVAPORATION TECHNIQUES FOR PREPARING RARE-EARTH TARGETS

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USED IN HEAVY-ION NUCLEAR PHYSICS

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Abstract

The preparation techniques for producing nuclear targets of the rare-earth isotopes depends greatly upon the physical properties of the particular rare-earth element. In most cases the isotope is supplied in the oxide form which then requires reduction to obtain the metal. Collection efficiencies will be discussed as this is of vital importance when considering the price and availability of the isotopic material.

1. Introduction

The preparation of nuclear targets of the rare-earth isotopes usually requires reducing them to the metallic form since these stable compounds are provided mainly as oxides. The method of reduction-distillation in vacuum of the oxide to metal used has been previously described by Kobisk and Adair [1]. The reducing agent used depends upon the evaporation technique employed and often a suitable reductant can be chosen by a thermochemical analysis.

Table I lists the melting point, vapor pressures and reduction temperature for the rare-earth elements. They may be roughly divided into two groups; the low-temperature lanthanides (Sm, Eu, Tm, Yb) and high-temperature lanthanides (La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu). Reagney and Reagney [2] describe two methods of evaporation depending on the temperature of reduction. For the low-temperature materials, resistive heating of a closed tantalum "pinhole" boat is

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used with lanthanum as the reducing agent. For the higher temperature oxides an electron heated tantalum crucible is needed and thorium or zirconium is used as the reducing agent. In these cases zirconium was employed as the reductant.

In addition to the details associated with the reduction and evaporation of these elements, there is the problem of oxidation of these evaporated materials. Often this is not a serious problem and can be avoided by evaporating onto a suitable backing. After the evaporation the system is vented to atmosphere using an inert gas and the targets are stored under vacuum [3]. Self-supporting foils can be prepared only by employing special techniques or equipment.

Furthermore, with the availability of enriched stable isotopes being uncertain and sometimes expensive, it becomes imperative to strive for the highest efficiencies possible during the evaporation and preparation of these targets. Rolling is often pursued since it provides the greatest efficiency. For evaporations onto backings, methods of recovery and collection are necessary to conserve a precious isotope.

2. Experimental Arrangement and Sample Preparation

2.1 Low-temperature reductions

For the preparation of low-temperature lanthanide targets, a Veeco Model VE-775 vacuum evaporator capable of multiple resistive evaporations was employed. This system, previously described [4], has been recently upgraded with a CII Cryo-torr 8 cryopump, providing a clean high-vacuum environment for target deposition. This system has a Kronos Model QM-311 quartz crystal thickness monitor, a thermocouple temperature probe and rotatable shutter. Capabilities also exist for substrate heating. The vacuum is monitored by an ion gauge, and is typically in the 10^{-6} torr range during deposition. A photograph of this apparatus appears in figure 1.

1

The most stable isotopic form of the lanthanide element is the oxide. Any volatiles contained in this oxide material are first driven off by heating in a platinum boat in air at 1000 C for about 10 min. [5] or, alternately, in an alumina crucible placed within a tube furnace at 1000 C for 2 hrs. [6]. This driving off of volatile impurities is a good precaution especially when dealing with isotopic material. The reducing agent is obtained as "fresh" fine filings from the crystal bar to prevent oxidation.

The rare-earth oxide to be reduced was first mixed with the reducing agent (Zr, La, Hf, etc.) using twice the stoichiometric amount and was then pressed into a pellet. The close contact of the materials within the pellet aids in a more complete reduction. The size of the pellet and hence the size of the boat is determined by the quantity of material necessary to produce the target of the required thickness. This can be approximately calculated based on the geometry of the evaporation. The pellet was placed within a tantalum boat fashioned from seamless tubing of either 6 or 8 mm in dia. and 4 cm in length, having a 1 mm dia. hole drilled in its center and pinched closed at both ends. The boat is then clamped between the high-current electrodes. A stainless steel heat shield was mounted directly above the boat orifice to reduce heat exposure to the substrate or in some cases, the backing foils.

Current was applied to the boat slowly at first to assist in outgassing. After the vacuum had sufficiently recovered, the evaporation proceeded until the desired thickness was attained as measured with the quartz monitor. A number of targets can be prepared in this way providing total efficiencies of few percent.

2.2 High-temperature reductions

For the reduction of higher temperature oxides of the rare-earths an electron heated crucible was necessary for evaporation of the metal. The apparatus employed for preparation of these targets consisted of a vertical

electron beam gun or "mortar" source mfg. by Veeco, GmbH, installed within a VRC Model 3117 vacuum evaporator [7]. Vacuum, maintained within low 10^{-6} torr pressure, is achieved by an oil diffusion pump and large-capacitance liquid nitrogen trap, and measured with an ion gauge. As above, film thickness was ascertained using a quartz crystal monitor. Within the system was included a rotating shutter and thermocouple temperature sensor.

The evaporant material was prepared as before with the pellet placed within the 6 mm dia. by 15 mm long tantalum crucible. The crucible was heated by electron bombardment within the mortar source using a high-voltage power supply modified to operate at 6 kW. Figure 2 shows a photograph of this arrangement.

3. Reducing Agents - Thermochemical Considerations

The reduction-distillation process [1] as applied to the lanthanide oxides makes use of reducing agents resulting in low vapor pressure oxides having similar thermodynamic properties. Table II lists four such agents, (Zr, Hf, Th and La), their melting point, vapor pressures and enthalpy of formation. This is by no means an exhaustive list, others include Al, Ca, Ti, Y, and Ta. Although of those listed in the table, lanthanum possesses the largest enthalpy, it is not always the best reductant for the evaporation of high-temperature rare-earth oxides. A thermodynamic analysis requiring a minimum change in free energy for the reduction process is a better guide in the choice of a suitable reducing agent as has been shown in the case of calcium [5].

3.1 Lanthanum

Samarium is an example of a rare-earth having a low melting point. Table 3 lists the free energy change of the reactions involving several reducing agents. The temperature of reduction, 1573 K obtained by Westgard & Bjornholm [8], was used for the calculations. From the analysis it can be seen that the lowest

free energy change per mole of Sm would be obtained by using thorium as the reductant. Thorium was not considered due to its toxicity as well as its low radioactivity level. ZrO_2 gives 22.3 kcal and HfO_2 gives 19.1 kcal for the reactions written.

Lanthanum then has the next lowest free energy change using these calculations (6.7 kcal) and was chosen to be the reducing agent for Sm_2O_3 . The temperature of the reduction must be kept as low as possible in order not to vaporize the lanthanum and contaminate the target. Targets of 0.1 - 0.7 mg/cm² $^{144}, ^{150}, ^{152}, ^{154}Sm$ have been produced using this technique deposited on carbon backings of 15 & 20 $\mu g/cm^2$ and Pb backings of 50 mg/cm². The efficiencies for these evaporations varied from 0.9% to 1.6%, this includes the efficiency of the reduction. Figure 1 shows the arrangement used for Sm deposited onto carbon backings (4 shown).

Thin targets of terbium, which is mono-isotopic, having a thickness of 14 $\mu g/cm^2$ on 2 $\mu g/cm^2$ carbon foils were prepared in a similar fashion, also using lanthanum as the reducing agent.

3.2 Zirconium

Neodymium is an example of the high-temperature oxides. Table 4 gives the free energy change for the various reactions involving the above reducing agents and neodymium oxide. The calculations were carried out using the temperature of reduction of 2073 K as given by Pengo [6]. One can then compare the free energy change per mole of Nd for each of the equations written. The reaction temperature is high enough though to cause some thorium evaporation to contaminate the target, thus requiring a further distillation. Each re-distillation/re-evaporation also lowers the efficiency, as was observed with gadolinium [1].

Lanthanum can be eliminated since it would melt before reaching the temperature needed to reduce the neodymium oxide. It should be noted that, thermochemically, zirconium (7.8 kcal per mole Nd) is less favorable than hafnium (3.9 kcal per mole Nd) as a reductant. This was rather surprising since traditionally Zr has always been used as a reducing agent in the past [5]. Recent work by Pengo et al [6] finds Hf to work for all of the rare-earths, obtaining reasonable efficiencies.

Using this method, with zirconium as the reducing agent, targets of ^{146}Nd of thickness 0.5 and 1.2 mg/cm² have been prepared on 500 $\mu\text{g}/\text{cm}^2$ carbon backings. The efficiency for these depositions was 2.0-2.5%.

4. Some Additional Target Preparation Examples

4.1 Ytterbium targets

Using the method described above for low-temperature reductions, targets of ^{176}Yb of 300 $\mu\text{g}/\text{cm}^2$ on 100 $\mu\text{g}/\text{cm}^2$ Au backings were prepared. The ytterbium was deposited directly onto gold coated glass slides and the targets floated off in water. Collection efficiency on the slides exceeded 33%. Extreme care is required so as not to submerge the Yb coating. The targets are then rinsed in methanol and dried. These targets have been successfully stored under vacuum for some period of time. Targets of 1 to 1.5 mg/cm² ^{176}Yb on mounted 50 mg/cm² lead foils were produced in a similar fashion by direct evaporation onto the backings.

Self-supporting foils of 300 $\mu\text{g}/\text{cm}^2$ ^{176}Yb were prepared as described by Yaraskavitch and Peng [9] using collodion to protect the foil while floating. Many targets were prepared this way with a success rate of 80%. An attempt was made to produce Er and Dy targets using this technique with no success. This work is still in progress.

4.2 Gadolinium targets

Gadolinium has proved to be a most difficult target to fabricate. Targets of up to 1 mg/cm^2 of natural Gd deposited onto a "stretched" Au substrate [10] of 1.5 mg/cm^2 foil thickness have been produced using the mortar source described above with Zr as the reducing agent. Total efficiency of 3.0% has been achieved for this deposition, assuming total reduction of the oxide. Nevertheless, a thin tantalum sheet is placed below the target holder in order to collect any isotopic material not deposited on the substrate. This material can be recovered for further use. A target of $500 \text{ } \mu\text{g/cm}^2$ ^{150}Gd on a "stretched" gold substrate was prepared in this manner as well as ^{148}Nd targets. The photograph in figure 2 depicts the set-up for the reduction of gadolinium. The stretcher frame may be seen and is rotatable into the evaporation stream. The source to substrate distance is 2.5 cm. Additionally, the reduced material has been collected on a quartz dome using the mortar and then re-evaporated onto carbon backings with the electron beam evaporator system previously described [7]. To date, using zirconium as the reducing agent, collection efficiencies of 60% have been achieved. The technique of using a resistively heated Ta boat with Hf as the reductant [6] is being investigated.

5. Conclusion

In conclusion, for preparing targets of the low melting point rare-earths deposited onto backing foils, a resistively heated closed Ta boat is used with La as the reducing agent. Isotopic targets of Sm, Tb and Yb have been made in this way. For the higher temperature lanthanides, the method of using an electron heated crucible in a mortar source was found to be successful, using Zr or Hf as the reductant. Targets of $^{146}, ^{148}\text{Nd}$ on carbon and gold backings, respectively, have been produced. Work on the reduction and collection of ^{160}Gd for the preparation of nuclear targets is continuing.

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Figure Captions

Fig. 1. Photograph of experimental arrangement for the reduction-distillation of samarium onto 20 $\mu\text{g}/\text{cm}^2$ carbon backing foils.

Fig. 2 Photograph of experimental arrangement for the reduction-distillation of gadolinium onto a 1.5 mg/cm^2 "stretched" gold substrate.

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Table Captions

Table I. Characteristics of the rare-earth elements. The reduction temperatures are using hafnium as the reducing agent.

Table II. Characteristics of the different reducing agents. The enthalpy given in the last column refers to the oxide.

Table III. Calculation of the free energy change for the metallothermic reduction of samarium.

Table IV. Calculations of the free energy change for the metallothermic reduction of neodymium.

Table I

Rare-Earth Element	Melting ^{a)} Point (°C)	Temperature(°C) @ Vapor Pressure(Torr) ^{b)}				Reduction ^{c)} Temperature (°C)
		10 ⁻⁸	10 ⁻⁷	10 ⁻⁶	10 ⁻⁵	
Lanthanum	920	1022	1102	1192	1297	1750
Cerium	795	972	1052	1147	1252	1750
Praseodymium	931	797	867	947	1042	1650
Neodymium	1024	727	797	862	947	1800
Samarium	1072	371	415	465	517	1400
Europium	822	283	319	361	409	1200
Gadolinium	1312	762	827	897	977	1800
Terbium	1357	797	867	947	1042	1800
Dysprosium	1409	625	682	747	817	1750
Holmium	1470	649	708	777	852	1750
Erbium	1497	649	708	777	852	1600
Thulium	1545	458	503	552	609	1650
Ytterbium	824	247	279	317	365	1200
Lutetium	1625	912	987	1072	1167	1750

a)Ref. 11

b)Ref. 12

c)Ref. 6

Table II

Reducing Agent	Melting ^{a)} Point (°C)	Temperature(°C) @ Vapor Pressure(Torr) ^{b)}				Enthalphy ΔH^c) Temperature (°C)
		10 ⁻⁸	10 ⁻⁷	10 ⁻⁶	10 ⁻⁵	
Zirconium	1852	1482	1582	1702	1837	-264
Hafnium	2150	1487	1592	1707	1847	-268
Thorium	1700	1432	1542	1662	1807	-294
Lanthanum	920	1022	1102	1192	1297	-431

a)Ref. 11

b)Ref. 12

c)Ref. 6

Table III

Metallothermic Reduction of Samarium*	Free Energy Change (kcal)	F.E.C. Per Mole Sm (kcal)
$3\text{Zr} + 2\text{Sm}_2\text{O}_3 + 3\text{ZrO}_2 + 4\text{Sm}$	89.0	22.3
$3\text{Hf} + 2\text{Sm}_2\text{O}_3 + 3\text{HfO}_2 + 4\text{Sm}$	76.3	19.1
$2\text{La} + \text{Sm}_2\text{O}_3 + \text{La}_2\text{O}_3 + 2\text{Sm}$	17.3	6.7
$3\text{Th} + 2\text{Sm}_2\text{O}_3 + 3\text{ThO}_2 + 2\text{Sm}$	101.2	10.6

*Calculations made for Temp. at 1573 K.

Table IV

Metallothermic Reduction of Neodymium*	Free Energy Change (kcal)	F.E.C. Per Mole Nd (kcal)
$2\text{La} + \text{Nd}_2\text{O}_3 \rightarrow \text{La}_2\text{O}_3 + 2\text{La}$	25.7	12.9
$3\text{Zr} + 2\text{Nd}_2\text{O}_3 \rightarrow 3\text{ZrO}_2 + 4\text{Nd}$	31.1	7.8
$3\text{Hf} + 2\text{Nd}_2\text{O}_3 \rightarrow 3\text{HfO}_2 + 4\text{Nd}$	16.0	4.0
$3\text{Th} + 2\text{Nd}_2\text{O}_3 \rightarrow 3\text{ThO}_2 + 4\text{Nd}$	-53.7	-13.4

*Calculations made for Temp. at 2073 K.

Fig. 1

Fig. 2

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