Exploration and Methods in the Production of Reduced Metals and Fluorinated Rare Earth Elements

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Introduction

With new technology on the rise and increased production of stable isotopes, researchers around the world are in need of rare enriched stable isotopes and made-to-order nuclear targets. Because of this, the Stable Isotope Materials and Chemistry (SIMC) group at ORNL focuses on operations of R&D equipment to provide custom-fabricated, isotopically enriched materials to customers worldwide. Some of their focuses include the production of nuclear targets as well as the reduction of isotopic materials. Two processes that SIMC is currently looking at are the fluorination of Rare Earth Elements (REE) and the Van Arkel-de Boer Process. Current methods for the reduction of REE involve the use of hydrofluoric acid which poses extreme safety hazards and requires specialized training. Because of this, researchers are turning to ammonium bifluoride (NH_4HF_2) as a chemical of interest for the fluorination of REE to produce reduced REE. The Van Arkel-de Boer process, also known as the iodide process, is a method used for the purification and reduction of titanium and other transition metals. This method can reduce various metals and create high purity, ductile crystals which increases the usability of the metal for different application. High ductility improves the metals versatility, allowing it to be shaped in various forms without compromising its tensile strength.

Fluorination

Background for Fluorination

- Attainment of reduced REE (Gd, Nd, Lu, Eu) are crucial for various research experiments and modern technology
- REE have distinct properties that make them important in nuclear targetry, scintillation material, nuclear batteries, permanent magnets, etc.

Figure 1: Tube furnace

Experiment

- Dry REE oxide in box furnace (800°C) to remove excess moisture
- REE is mixed with ABF in a 1:8 molar ratio
- Place sample in quartz tube furnace, flow with Ar and set to specific heat profile
- REE fluoride is then sent to material lab where the fluoride is reduced with Ca

Heating Profile and Chemical Equations:

Tube Furnace @ 200°C -

$$R_2O_{3(s)} + 6NH_4HF_{2(s)} \xrightarrow{\Delta} 2NH_4RF_{4(s)} + 4NH_4F_{(g)} + 3H_2O_{(g)}$$

Tube Furnace @ 800°C -

$$NH_4RF_{4(s)} \xrightarrow{\Delta} RF_{3(s)} + NH_4F_{(g)}$$

(a) (b) (c) (d)

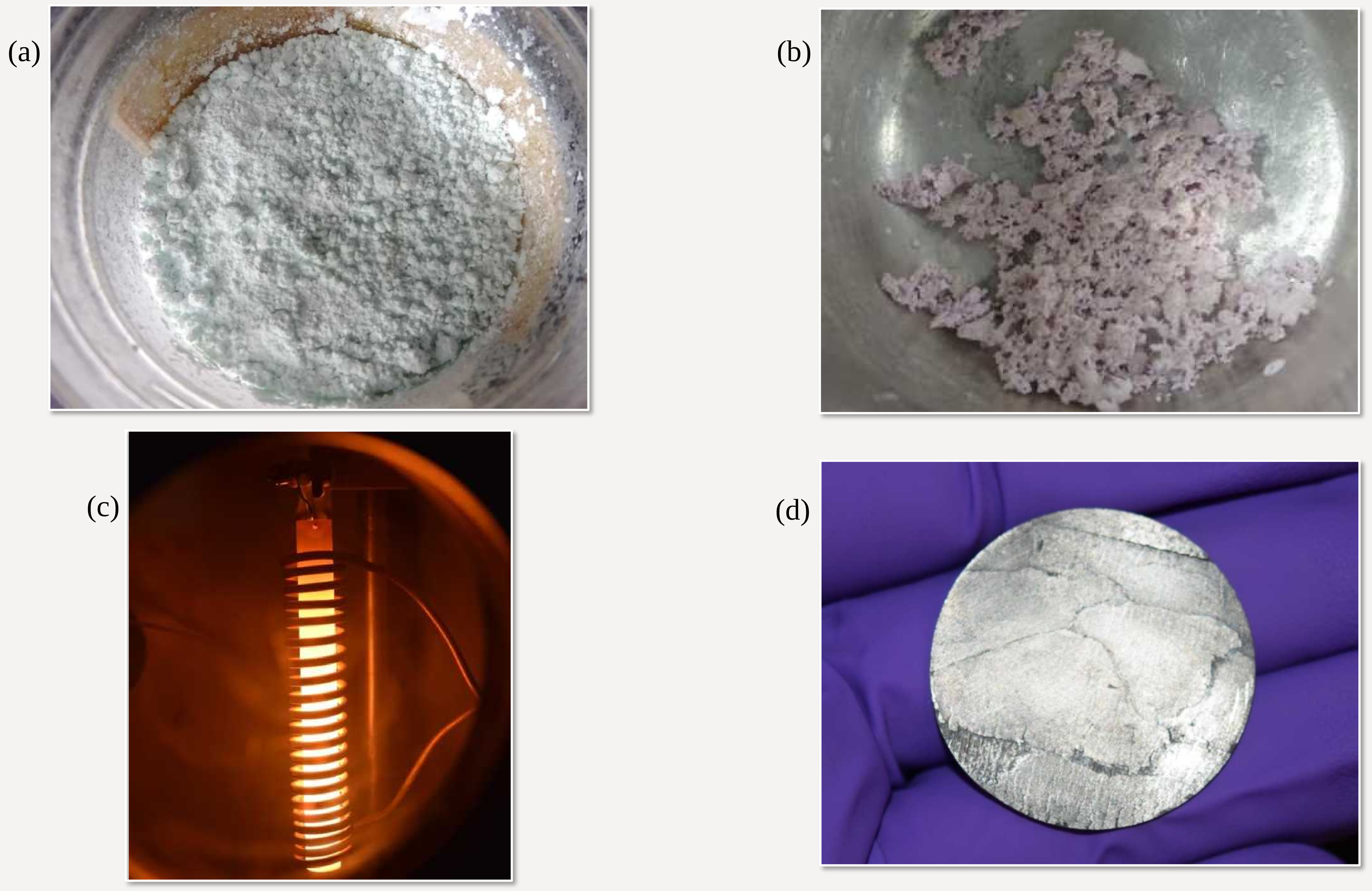

Figure 2. Process of REE fluorination - (a) Neodymium oxide (Nd_2O_3) (b) Neodymium fluoride (NdF_3) (c) Reduction of REE fluoride with Ca in inductive heating system under vacuum (d) Final desired product – cold rolled Gd disk

Fluorination Results

SEM Results

- Sample material, after fluorination, appears to be pure GdF_3

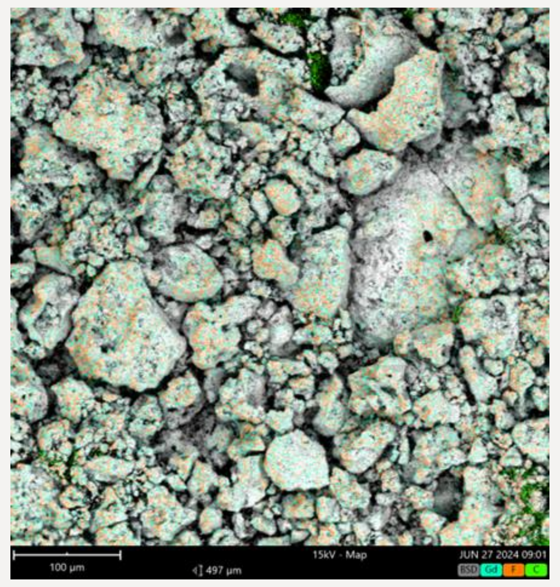

Figure 3: SEM map of elemental distribution of GdF_3 sample

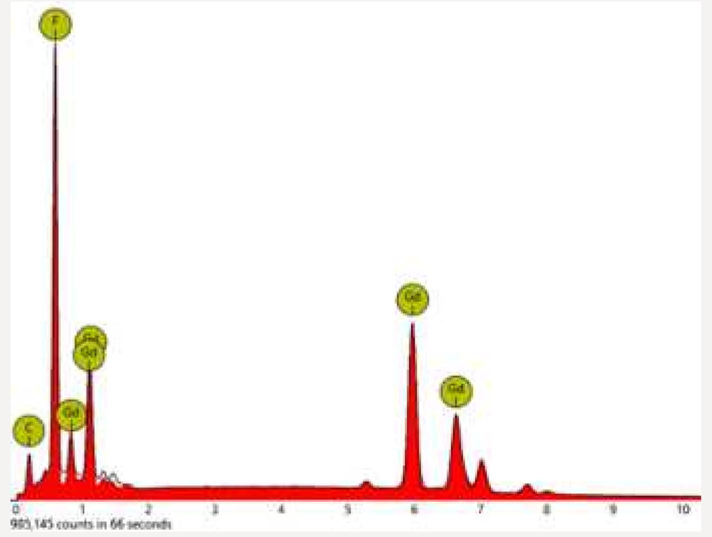

Figure 4: Composition analysis of Fig. 7

PXRD Results

- Dark blue lines show expected peaks for GdF_3
- Light blue lines show expected peaks for Gd_2O_3
- Red peaks correlate with dark blue lines representing GdF_3

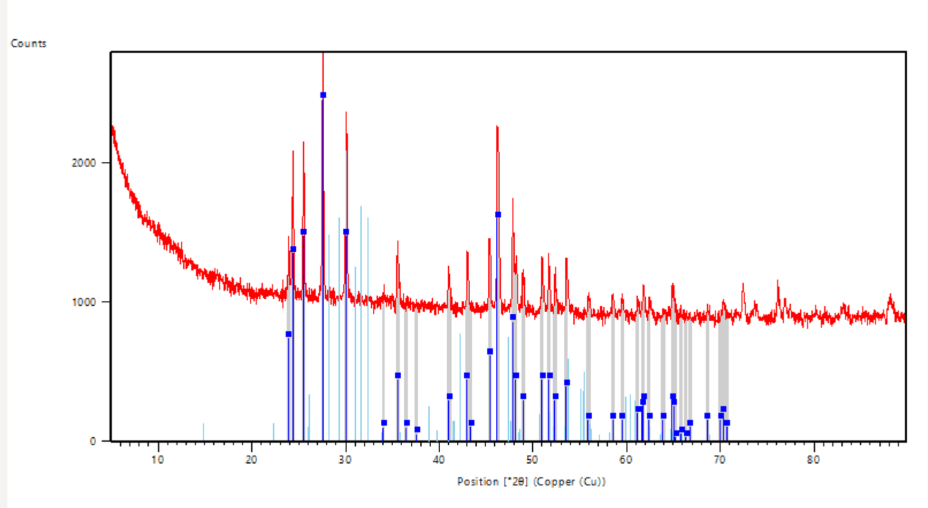

Figure 5: PXRD analysis of fluorinated Gd sample

Crystal Bar

Background for Van Arkel-de Boer process

- In a system under vacuum, iodine ($I_{2(s)}$) and a transition metal are heated to ~200°C, where iodine sublimates
- The iodine gas reacts with the metal to form volatile metal tetraiodide (MI_4)
- The volatile metal iodine undergoes sublimation at elevated temperatures, separating impurities, and depositing high-purity metal onto a hot filament
- Previous methods using this process are typically expensive and time consuming (4-8 days)
- New method would allow in-house production with option to scale up

Figure 6: Vacuum system

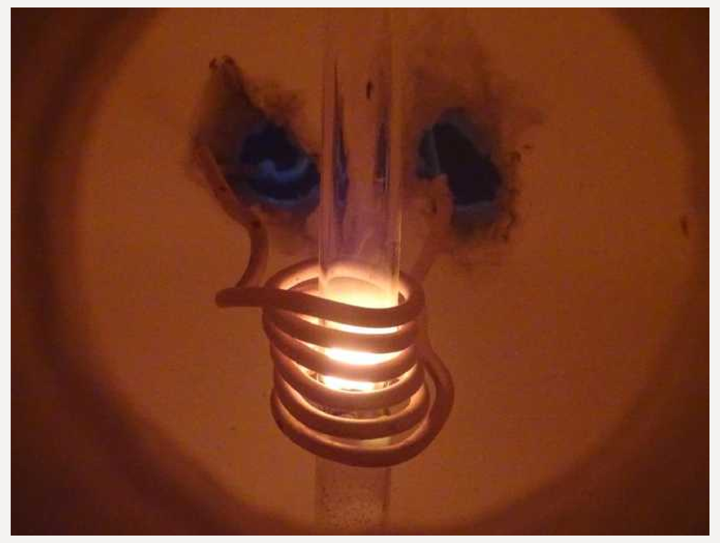

Figure 7: Susceptor at 1200°C

Improvements

- Small scale quartz tubing that can be flame sealed in-house, eliminating the need for a glass shop
- Simple Setup - Dual conventional box furnace and induction heating system
- Switch tungsten filament for a graphite susceptor for affordability and ease in machining
- Adjustability for different quartz tube sizing due to interchangeable coils
- Allows for small minimum batch sizes

Experiment

- Use ¼" quartz tube and flame seal in low vacuum
- Various sample sizes of titanium (Ti) and iodine (I_2) used to find most efficient ratio of Ti:I_2 needed
- Adjust temperature and amperage to maximize titanium tetraiodide (TiI_4) production

Heating Profile and Chemical Equation:

Heat Profile: Susceptor @ 1200°C, Box Furnace @ 600°C

$$Ti_{(s)} + 2I_{2(g)} \xrightarrow{\Delta} TiI_{4(g)} \xrightarrow{\Delta} Ti_{(s)} + I_{2(g)}$$

Figure 8: Iodine gas in ampoule

Crystal Bar Results

SEM Results

- Fig. 9 shows contamination of Si on susceptor
- Potentially from devitrification from quartz tube
- Fig. 11, shows Ti crystal growth with no oxidation

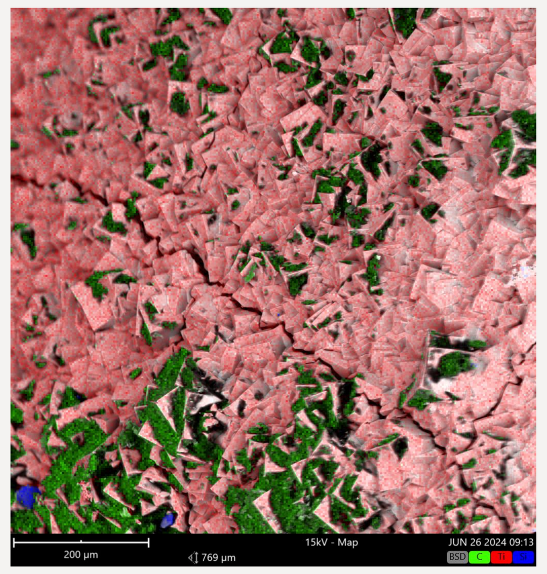

Figure 9: SEM map of surface topography of Ti crystals

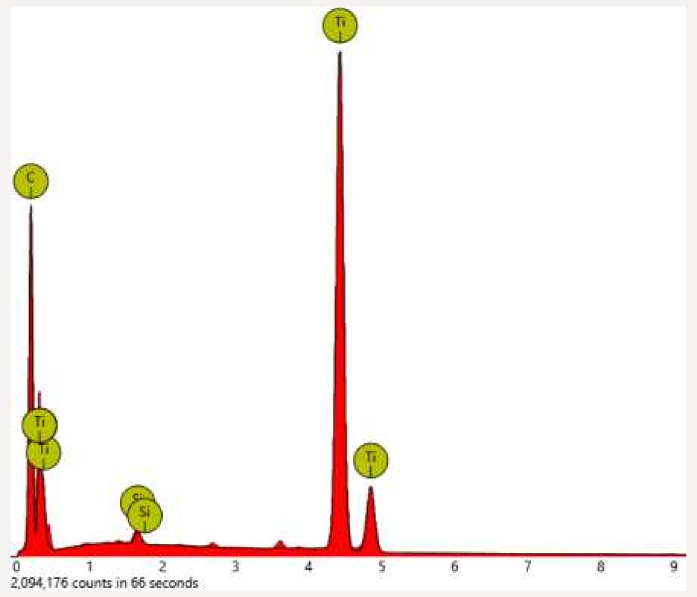

Figure 10: Composition analysis of Figure 9

PXRD Results

- Blue/Green lines correlate with red lines potentially represents Ti/TiO

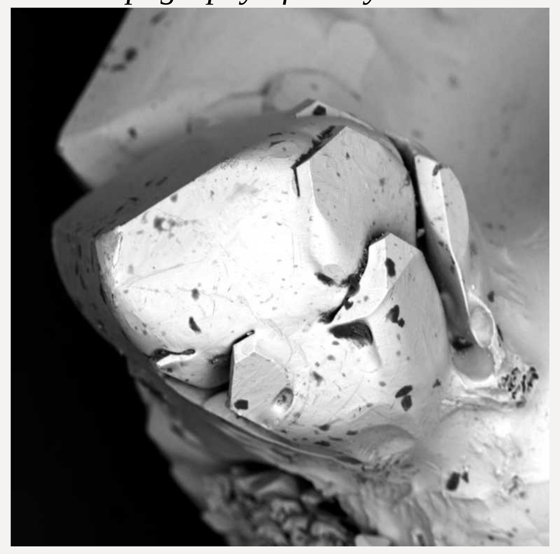

Figure 11: Enlarged SEM view of Ti crystal growth

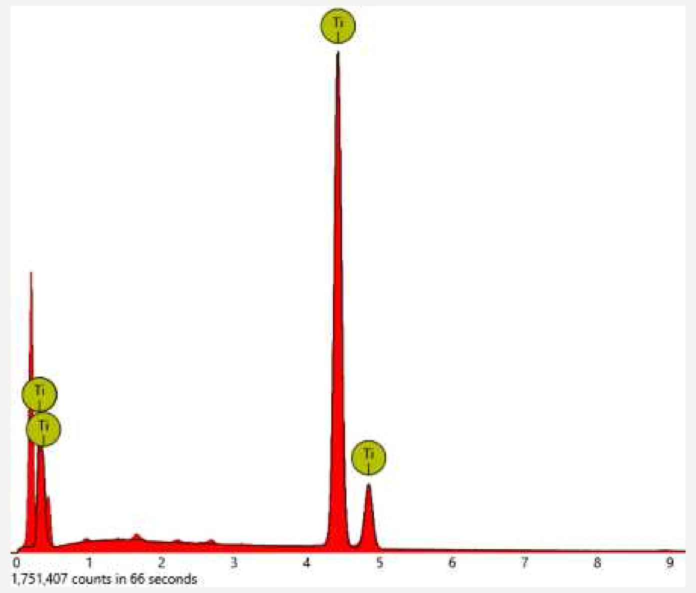

Figure 12: Composition analysis of Figure 11

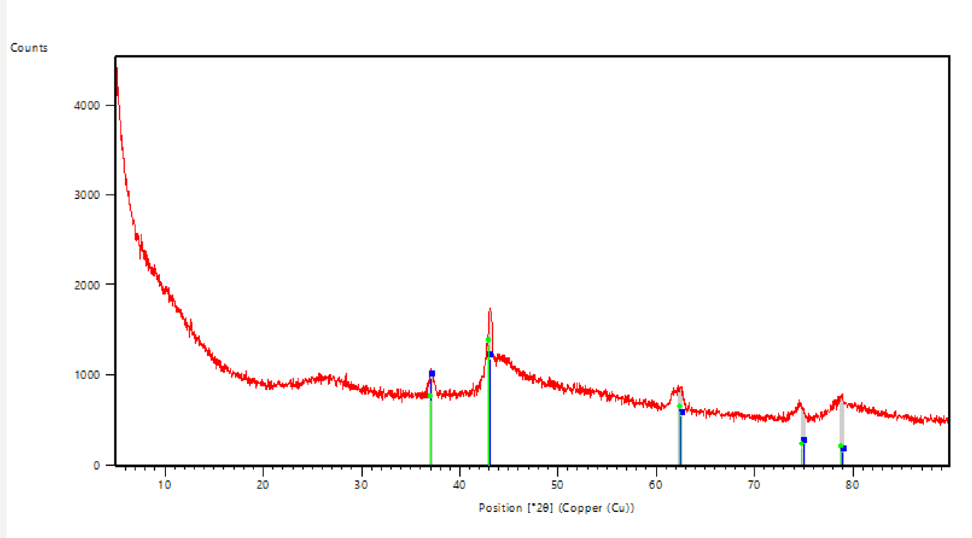

Figure 13: PXRD analysis of susceptor

Figure 14: Ti crystals on graphite susceptor

Future Work

Fluorination

- Continue reduction of fluorinated REEs with calcium

$$2RF_{3(s)} + 3Ca_{(s)} \xrightarrow{\Delta} 2R_{(s)} + 3CaF_{(g)}$$

- Improve reaction vessel for fluorinated REE + Ca to decrease loss of material
- Attempt to make nuclear targets out of reduced REEs

Crystal Bar

- Continue improvements on design of quartz ampoule
- Attempt this process with various other metals including Si, Zr, and Hf
- Adjust system to accommodate various ampoule sizes, allowing for scale up to gram quantities

Acknowledgments

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HIPPO Horizon-Broadening Isotope Production Pipeline Opportunities

Isotope Program U.S. Department of Energy