Investigating Reduction Techniques for TiO_2 to Ti Metal

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This work was supported in part by the Horizon-Broadening Isotope Production Pipeline Opportunities (HIPPO) program under Grant DE-SC0022550 from the Department of Energy's Isotope R&D and Production Program

Introduction

Why Ti Metal?

- Titanium is vital for industry; Kroll method (industrial reduction method) is costly and energy-intensive.
- Natural titanium commercially available; Isotopically enriched titanium must be reduced from its oxide separately.
- Enriched Ti isotopes have varying oxygen tolerance (0-1%)
- Minimizing material loss is crucial due to the high cost
- Solid Hydride CaH_2 reduction is simpler and high-yield but not suitable for ductile applications
- Hydrogen-Assisted Magnesiothermic Reduction process has promising industrial applicability

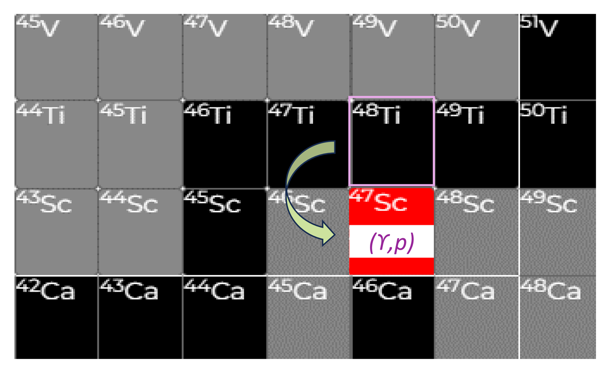


Table 1: Simulated decay of ^{48}Ti to ^{47}Sc through (Y,p) reaction used for medical applications.

Methods

Solid Hydride CaH_2 (Calciothermic) Reduction

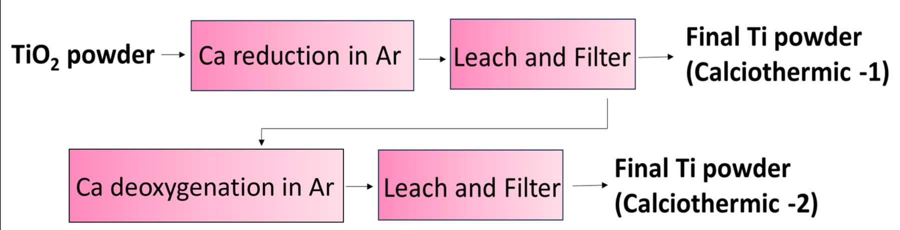


Figure 1: Flowchart of solid hydride CaH_2 Reduction Process.

Figure 3: Furnace set-up of solid hydride CaH_2 Reduction Process.

- Combined TiO_2 with CaH_2 powder heated to 1000 °C for 90 minutes under Ar flow

- Reduced powder leached in glacial acetic acid to produce slurry solution
- Solution filtered under vacuum with isopropanol and distilled water
- Filtered powder dried in oven at 80 C °for 30 minutes

Figure 4: Vacuum filtration unit set-up for natural Ti powder.

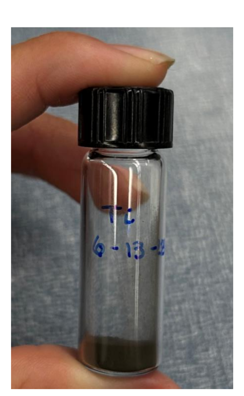


Figure 5: Calciothermic- 1 post-reduction powder.

- Calciothermic – 1 (treated powder) mixed with CaH_2 for deoxygenation process
- Treated powder and CaH_2 mixture heated to 1000 °C for 90 minutes under Ar flow
- Leaching and Filtering Process same as above

Hydrogen Assisted Magnesiothermic Reduction (HAMR)

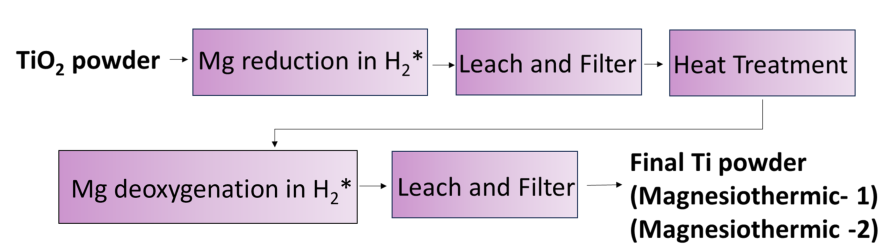


Figure 2: Flowchart of HAMR Process.

Figure 6: Furnace set-up of HAMR Process.

- TiO_2 combined with Mg metal and $MgCl_2$
- Powder pressed into pellets and transferred to Mo crucibles and heated to 900 °C for 90 minutes under H_2* flow

- Reduced powder leached in HCl to produce slurry solution
- Solution filtered under vacuum with isopropanol and distilled water
- Filtered powder dried in oven at 80 C °for 30 minutes

Figure 7: Combined TiO_2, Mg metal, and $MgCl_2$ pellets in crucible before reduction process.

** Non- flammable Hydrogen*

Figure 8: Magnesiothermic – 2 post-reduction powder.

- Reduced powder pressed into pellets and heated to 900 °C for 45 minutes under H_2* flow
- Heat-treated powder recombined with Mg and $MgCl_2$
- Powder pressed into pellets and heated to 720 °C for 90 minutes under H_2* flow
- Leaching and Filtering Process same as above

Challenges and Limitations

Particle Size

- Unreacted Mg metal from over-adding reactant
- Mg metal pellets exhibited large surface area making it difficult to fully reduce during reaction and leach out

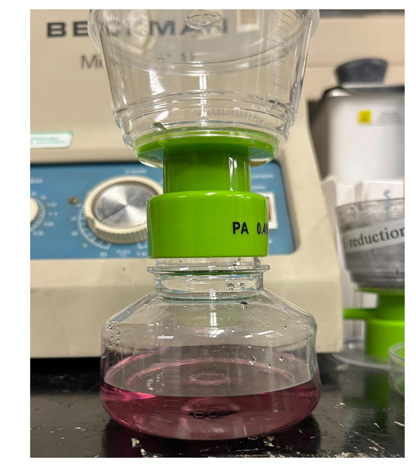
Figure 9: Unreacted Mg metal pellet pieces post-HAMR deoxygenation.

Dissolution Efficiency

- HCl used to further reduce oxygen content
- Leaching with HCl (0.01, 0.1, 0.32 M) leaves undissociated MgO and undissolved Mg metal
- Time of leaching with HCl extended up to two days with no notable improvement
- Effective leaching process seen with glacial acetic acid

Figure 10: Leaching process using glacial acetic acid and 0.01 M HCl for HAMR.

Acid Strength



- Stronger molarity HCl was tested for more effective leaching process
- High molarity HCl easily dissolves Ti metal producing a violet solution
- HCl molarity requires further optimization

Figure 11: Filtration of HAMR powder with 12.1 M HCl.

Results

Calciothermic Reduction Method

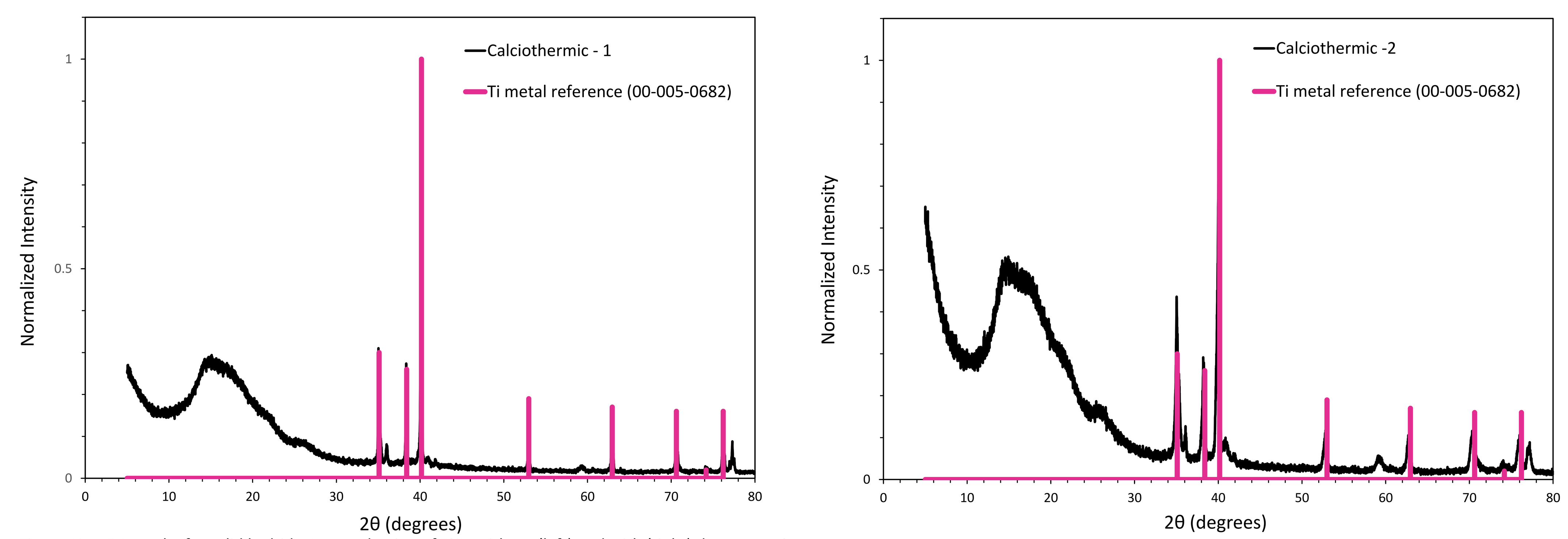


Figure 12: XRD results for solid hydride CaH_2 reduction of TiO_2 without (left) and with (right) deoxygenation process.

- Models show qualitative agreement to Ti metal reference for successful conversion of TiO_2 to Ti metal without significant impurities
- No notable variation between models signifying potentially redundant deoxygenation process
- Residual oxygen (<5wt%) present in minimal quantities, not significantly affecting overall purity of Ti metal
- Unidentified peaks imply potential contamination in producing pure titanium metal

Magnesiothermic Reduction Method

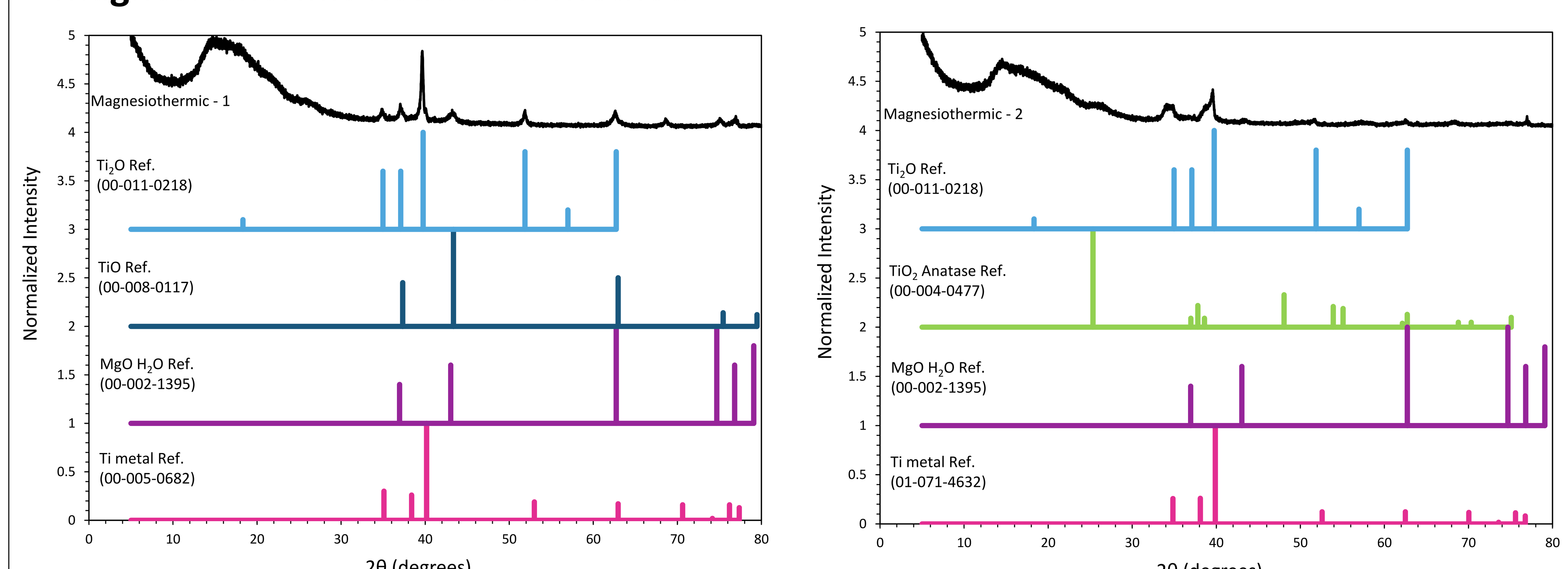


Figure 13: XRD results for HAMR of TiO_2.

- XRD results exhibit limited qualitative agreement with Ti metal reference and predominant alignment with intermediate Ti_2O phase, indicating an incomplete reduction
- Residual MgO H_2O are detected in both sample stages, indicative of insufficient leaching
- Magnesiothermic – 2 model (right) demonstrates broad peaks implying a semi-crystalline structure
- Unidentified peaks imply potential contamination in producing pure titanium metal

Conclusions

- Calciothermic reduction is a robust and efficient technique for high-yield titanium metal production
- No significant improvement observed when Calciothermic reduction is combined with a deoxygenation process
- Additional experimental data is necessary to quantify the relative oxygen content in Calciothermic samples
- Magnesiothermic Reduction necessitates a more rigorous deoxygenation process to achieve titanium metal production

Future Work

- Enhance overall efficiency of Magnesiothermic reduction by employing powdered magnesium metal and pure hydrogen gas
- Optimize deoxygenation phase of Magnesiothermic reduction with varying HCl concentrations and the use of $MgCl_2$-bearing salts
- Investigate additional TiO_2 reduction techniques including vapor-Ca reduction and bomb reduction using sodium as a reactant
- Conduct further studies to characterize the reduction yield percentages and quantify the relative oxygen content for each reduction process

References

[1] B. Lommel, "Reduction of isotopically enriched ^{50}Ti-dioxide for the production of high-intensity heavy-ion beam", *Journal of Radioanalytical and Nuclear Chemistry*, 299:977-980, 2014, DOI 10.1007/s10967-013-2615-7

[2] Y. Zhang, "Hydrogen assisted Magnesiothermic reduction of TiO_2", *Chemical Engineering Journal*, 308, 299-310, 2017, DOI 10.1016/j.cej.2016.09.066