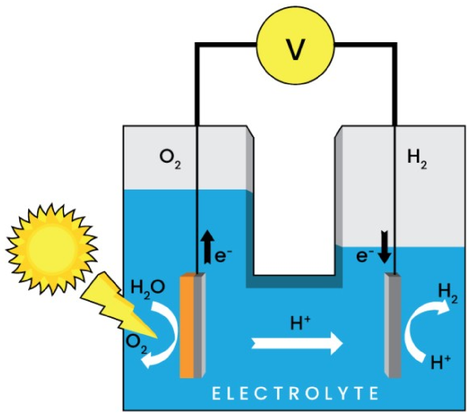
Synthesis of Transition Metal Nitrides

Luc Capaldi

The University of Vermont
College of Engineering & Mathematical Sciences
Department of Mechanical Engineering

I. Background



Since 2009, production of renewable energy has failed to keep pace with the nearly 61 EJ increase in global energy demand [1]. Photoelectrochemical devices that utilize solar energy to produce clean hydrogen fuel from water, are thus highly relevant to a sustainable future.

$$6Ta + 5N_2 \rightarrow 2Ta_3N_5$$

Various transition metal nitrides posses the correct photovoltaic properties to create such a device [2]. The 3:5 phase of tantalum nitride is a particularly attractive candidate [3].

II. Results: Arc Melter

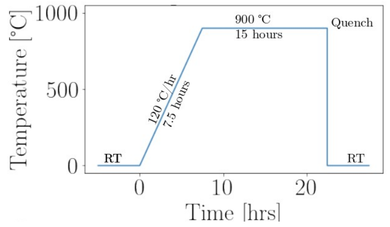
A subset of transition metal nitrides were arc melted under 1 atm of N_2 pressure. The following were selected based on abundance and non-volatility: Ti, V, Cr, Mn, Fe, Cu, Zr, Nb, Mo, and Ta.

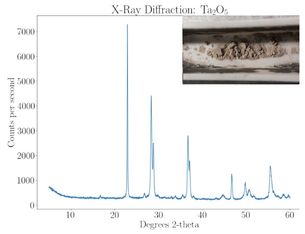
Both TiN and ZrN exhibit rock-salt structures while V_2N, Nb_2N, Ta_2N, and Cr_2N are all trigonal. Mo, Mn, Fe, and Cu did not form a nitride phase.

22 TiN	23 V_2N	24 Cr_2N
40 ZrN	41 Nb_2N	
	73 Ta_2N	

III. Results: Metallic Flux Method

Samples were heated in a Mini-Mite tube furnace under N_2 gas flow with the heating profile shown.

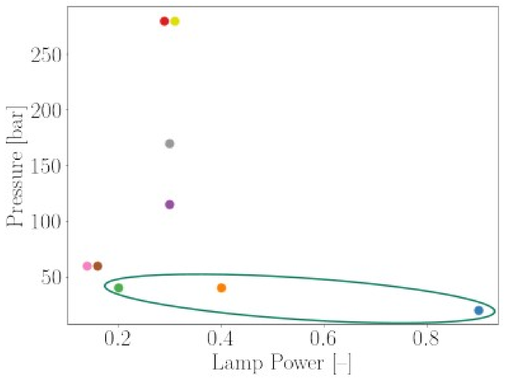




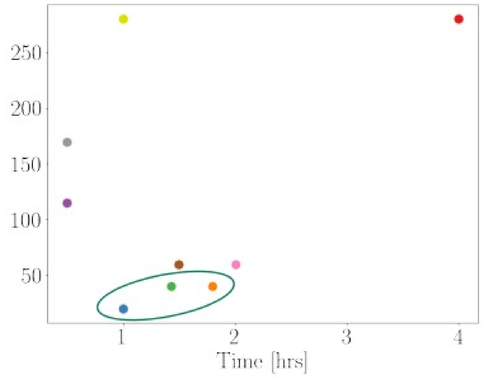
Pure Ta samples formed Ta_2O_5; When reheated, Ta_2O_5 samples changed color but not phase, indicating a reducing agent like H_2 is needed [4].

IV. Results: High Pressure Optical Floating Zone Furnace (HPFZ)

A series of experiments was conducted in the HPFZ with varying lamp power, pressure and reaction time. The circled points formed TaN phases.

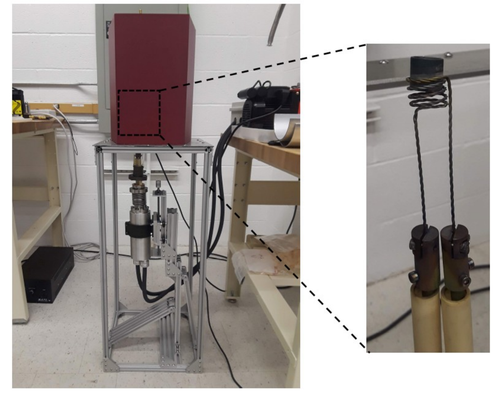


Nitride phases did not form for reaction times less than 1 hour or for lamp power less than 20-30%.



More advanced nitride phases did not form even at 280 bar, demonstrating that the HPFZ cannot directly access the 3:5 region of the phase space.

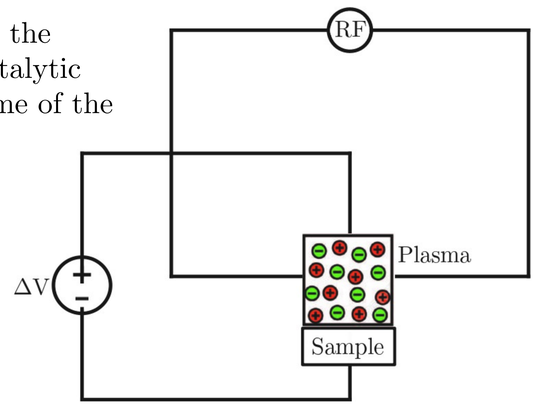
V. Future: Plasma Electrochemical Crystal Growth Furnace (PECG)



Future work will leverage a novel PECG furnace that uses electrochemical potential rather than pressure to access the phase space.

For nitride synthesis, the plasma provides a catalytic effect by splitting some of the N_2 triple bonds.

The applied DC voltage is used to tune the net electric field existing due to the electrochemical potential. This allows the reactivity to be controlled.



VI. Conclusions

1) TMN formation has been systematically investigated, showing excellent group-wise consistency.
2) Metallic flux experiments show that the $6Ta + 5N_2 \rightarrow 2Ta_3N_5$ reaction is not possible without an intermediary oxide phase (at the given thermodynamic state).
3) HPFZ experiments show that the 1:1 tantalum nitride phases are only formed for a reaction time above 1 hour and a lamp power above 20-30%

VII. Acknowledgments

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