

Synthesis of Transition Metal Nitrides

2021 JHU PARADIM REU

Luc Capaldi

*Department of Mechanical Engineering
College of Engineering and Mathematical Sciences
The University of Vermont*

(Dated: August 20, 2021)

Transition metal nitrides (TMNs) exhibit numerous desirable properties, including strong photovoltaic response and excellent material strength. This makes them viable for certain renewable energy applications. In this project, the phase and structural progression of various TMNs formed in an arc melter are investigated, with the results indicating a strong group-wise consistency. The formation of tantalum nitrides are further studied. Flux experiments show that the $6\text{Ta} + 5\text{N}_2 \rightarrow 2\text{Ta}_3\text{N}_5$ (3:5) pathway always includes an intermediate oxide phase, requiring a reducing agent such as H_2 to complete the reaction. Experiments in a High-Pressure Optical Floating Zone furnace indicate that 280 bar of N_2 is insufficient to access the 3:5 portion of the tantalum-nitrogen phase space directly, showing only the formation of $\varepsilon\text{-TaN}$ and $\delta\text{-TaN}$ for sufficiently large temperatures and reaction times. Future work will leverage a novel Plasma Electrochemical Crystal Growth furnace to explore a greater portion of the phase space.

I. Background

Global energy demand has increased by over 61 EJ since 2009, less than 25% of which may be attributed to renewable energies [1]. New technologies, such as photoelectrochemical devices that utilize solar energy to produce clean hydrogen fuel from water, are thus relevant for a sustainable future. These devices submerge an anode and cathode connected by a current-carrying wire in an ionic solution. Photons excite electrons on the surface of the anode, causing them to flow along the wire. The holes that remain are filled by breaking the O-H bonds in water, allowing the H cations to migrate to the cathode where they are reduced to form H_2 . Critically, this technology requires that the material terminals exhibit the appropriate photovoltaic response. Various transition metal nitrides are suitable for this application [2], of which Ta_3N_5 (3:5) is particularly attractive [3].

II. Arc Melter

The following subset of transition metals were selected based on abundance and non-volatility: Ti, V, Cr, Mn, Fe, Cu, Zr, Nb, Mo, and Ta.

22 TiN	23 V ₂ N	24 Cr ₂ N
40 ZrN	41 Nb ₂ N	
	73 Ta ₂ N	

FIG. 1. Transition metal nitrides formed during arc melting experiments.

Prior to each experiment, a standard evacuation cycle was performed, and a zirconium getter was melted to remove oxygen from the chamber. Under 1 atm of N_2 pressure, each sample was melted for 5 minutes. The phase and crystalline structure of each sample was examined using Powder X-Ray Diffraction (XRD) (see Figure 1). 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.

III. Metallic Flux Method

Powders were placed in an alumina crucible within a Mini-Mite tube furnace and heated to 900° at a ramp rate of 120°C/hr under N_2 flow and held there for 15 hours. The samples were then quenched by shutting off the furnace and the resulting phases characterized by Powder XRD. Pure Ta powder, originally held inside an Ar glovebox, was first studied. Only an intermediate oxide phase (Ta_2O_5) was obtained, demonstrating that a direct conversion to higher nitride phases is not possible at the given temperature and pressure. It has been reported that a reducing agent is needed to convert this oxide to higher nitride phases [4], so 5% H_2 in Ar gas was mixed in a 1:1 ratio with N_2 gas. Although the powder assumed a light brown coloration, a nitride phase was not obtained. It is possible that the input gas stream was contaminated with H_2O which drove the reaction in the opposite direction.

IV. High-Pressure Optical Floating Zone Furnace

A series of experiments were conducted in the High-Pressure Optical Floating Zone furnace (HPFZ) with pressed pellets of pure Ta powder. As shown in Figure 2, the high-pressure region of the tantalum-nitrogen phase space up to 280 bar has been thoroughly investigated. The results indicate that nitride reactions did not occur for either heat input below 20-30% lamp power (as a

function of the pressure) or for reaction times less than 1 hour. This holds at pressures up to 280 bar, demonstrating that the HPFZ cannot pressurize enough to directly access the 3:5 portion of the phase space. However, both δ -TaN and ϵ -TaN phases were consistently obtained when a sufficient heat input was provided at lower pressures.

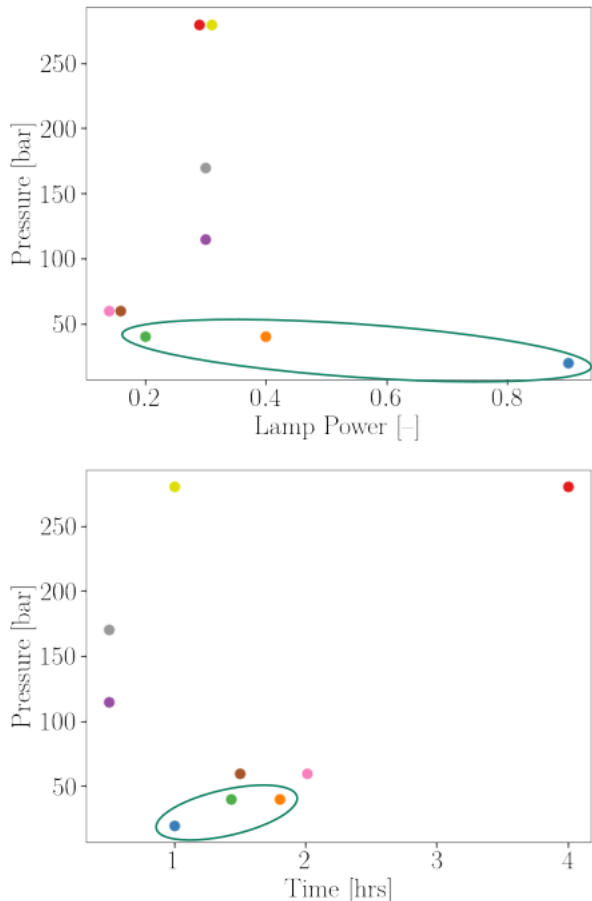


FIG. 2. Pressure as a function of the Lamp Power (**Top**) and the Time (**Bottom**), with color-coordinated data points. The circled points indicated the formation of TaN phases.

V. Conclusions

TMN formation has been systematically investigated, showing excellent group-wise consistency. In particular, the formation of tantalum nitrides has been studied with a variety of synthesis tools. The results showed that the $6\text{Ta} + 5\text{N}_2 \rightarrow 2\text{Ta}_3\text{N}_5$ reaction is not possible without an intermediate oxide phase, even at 280 bar. A direct

conversion at these pressures would likely necessitate a reducing agent like H_2 to convert the oxide to the desired phase. Floating zone syntheses will likely remain elusive until significantly higher pressures are available.

VI. Future Work: Plasma Electrochemical Crystal Growth Furnace

Future work will leverage a novel Plasma Electrochemical Crystal Growth furnace that uses electrochemical potential rather than pressure to explore the phase space. A prototype system features a vertically-oriented plasma furnace with a translating tungsten crucible-basket resistive heating element. This provides improved access to the phase space in three ways.

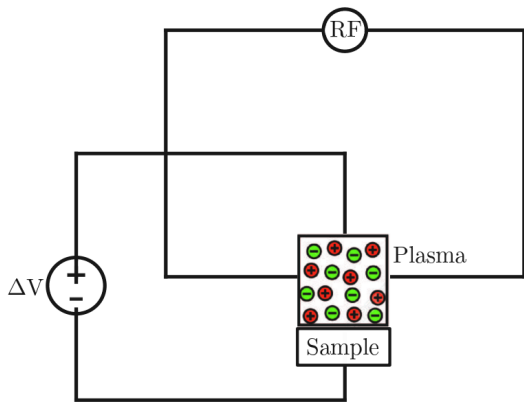


FIG. 3. Schematic showing the setup of the electrochemical crystal growth furnace.

i) For nitride synthesis, the plasma provides a catalytic effect by splitting some of the N_2 triple bonds. ii) The heating element allows the temperature to be changed. iii) The electrochemical potential between the electrically conductive plasma and sample is related to the reactivity. By varying an externally applied DC current, the net electric field – and thus the reactivity – may be precisely controlled. This will allow a larger portion of the phase space to be explored without the need for high pressures.

VII. Acknowledgements

Funding for this project is supported by the NSF (Platform for the Accelerated Realization, Discovery, Analysis and Discovery of Interface Materials (PARADIM)) under Cooperative Agreement No. DMR-1539918 as part of the Materials Innovation Platform Program.

[1] R. Secretariat, Renewables global status report (2021).
 [2] M.-S. Balogun, Y. Huang, W. Qiu, H. Yang, H. Ji, and Y. Tong, Updates on the development of nanostructured transition metal nitrides for electrochemical energy storage and water splitting, *Materials Today* **20**, 425–451 (2017).
 [3] J. Fu, F. Wang, Y. Xiao, Y. Yao, C. Feng, L. Chang, C.-M. Jiang, V. F. Kunzelmann, Z. M. Wang, A. O. Gov-

orov, and et al., Identifying performance-limiting deep traps in ta_3n_5 for solar water splitting, *ACS Catalysis* **10**, 10316–10324 (2020).
 [4] J. Cui, T. Liu, B. Dong, Y. Qi, H. Yuan, J. Gao, D. Yang, and F. Zhang, Flux-assisted synthesis of prism-like octahedral ta_3n_5 single-crystals with controllable facets for promoted photocatalytic h_2 evolution, *Solar RRL* **5**, 2000574 (2020).