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SAND2019-5484C

Controlled Atmosphere Plasma Spray (CAPS) and Cold Spray (CS) for High Purity Metal Deposits

ITSC 2019

Yokohama, Japan

PRESENTED BY

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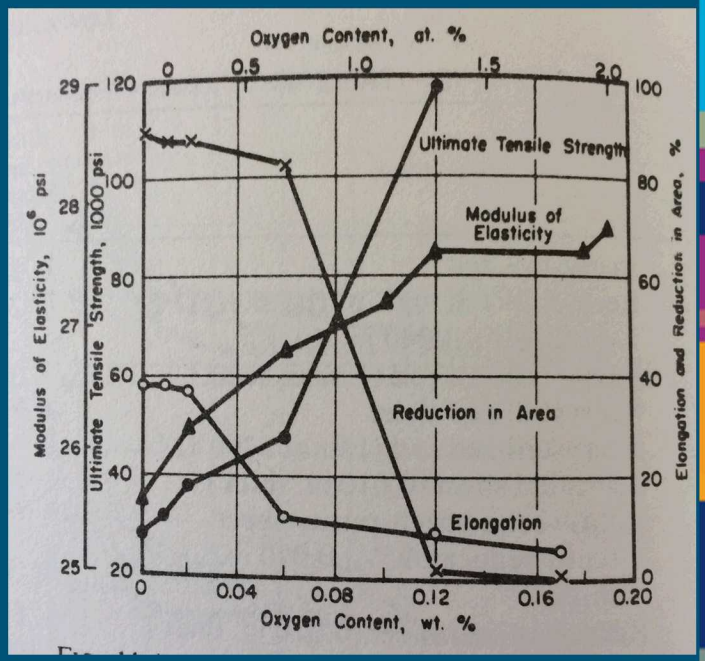
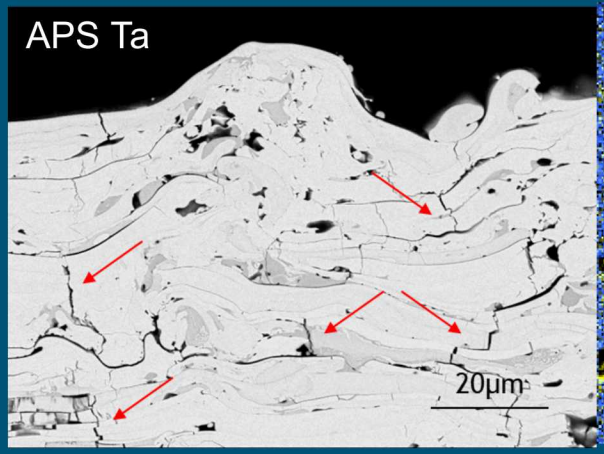
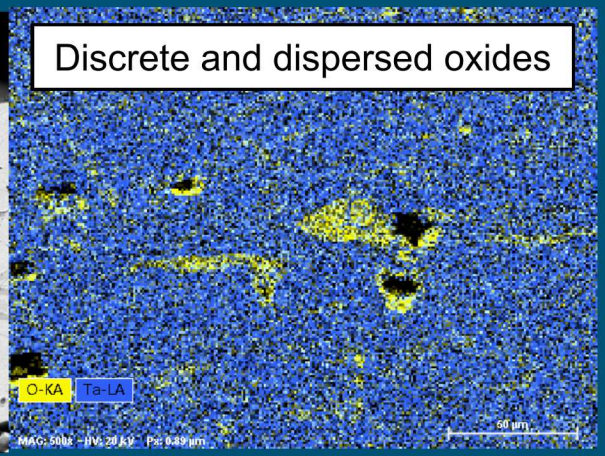
Motivation

- Significant change in mechanical properties in Ta, Nb with interstitial and/or compounds with O, N, and C may occur with processing and aging
- Thermal spray offers a useful tool for economically producing large area coatings or spray formed materials, but often involve chemical and/or phase changes during processing
- Early spray trials with Atmospheric Plasma Spray (APS) show heavy oxide inclusion, vertical microcracks from quenching stress



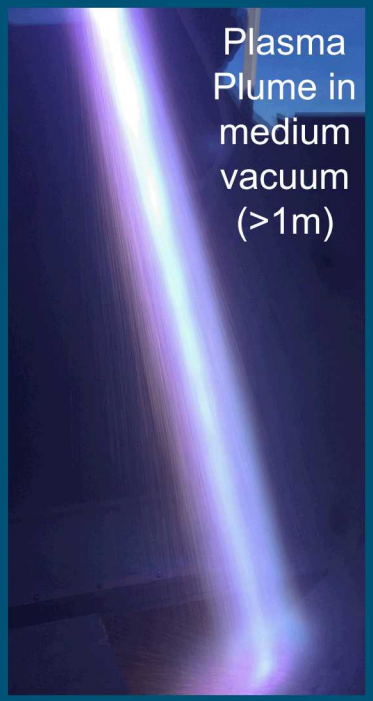
Kohl, Walter Heinrich. "Handbook of materials and techniques for vacuum devices." (1967).

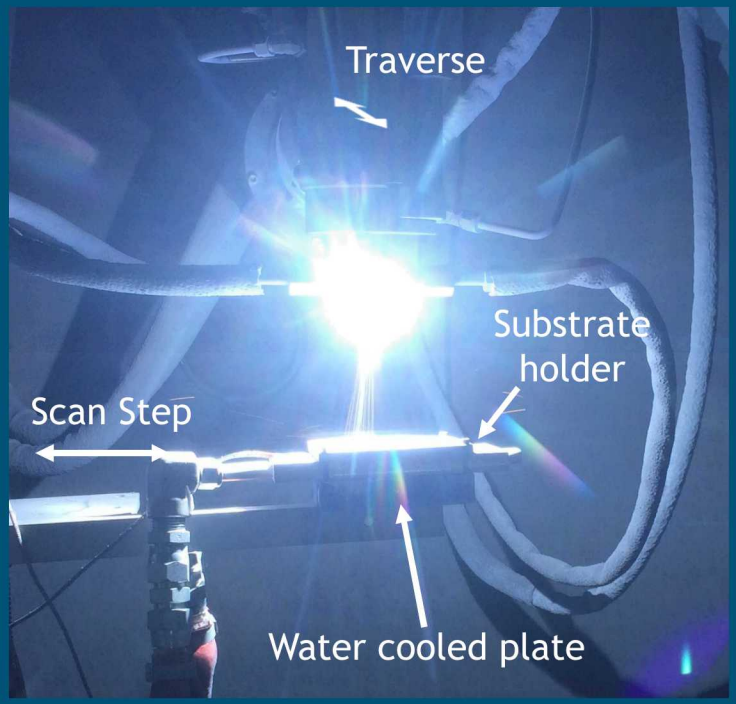




Air vs. Controlled Atmosphere Plasma Spray

- APS is inexpensive, common in industry
  - Ideal for oxides
  - Metal processing can result in un-desired oxidation, chemical uptake
- Controlled Atmosphere Plasma Spray (CAPS) provides an advanced processing tool
  - Recently refurbished capability at Sandia
  - Spray environments include medium vacuum (~5 to 10 torr) or inert gas backfill (Nitrogen or Argon from ~5 torr to atmospheric)
  - Reduces undesired metallic feedstock oxidation





Tantalum Interactions with Process Gases and Environment

Nitrogen
- Absorption and Nitride formation ($TaN_{0.05}$, Ta_2N, $TaN_{0.8\text{-}0.9}$, TaN, TaN_2)
- Nitride decomposition and outgassing of N_2 below melting point
- Hardness increases with Nitrogen content (greater than Oxygen)

Oxygen
- Absorption and Oxide formation (TaO, Ta_2O_4, Ta_2O_5)
- Ta_2O_5 forms >600°C, decomposes at 1470°C, outgassing at higher temperatures
- Hardness increases, ductility reduction

Hydrogen
- Absorption and Hydride formation ($TaH_{0.74}$)
- Absorption >250°C, H_2 release in vacuum >800°C, all released by 1300°C in vacuum
- Embrittlement

Argon, Helium
- No reactions – **Ideal Processing Gases**

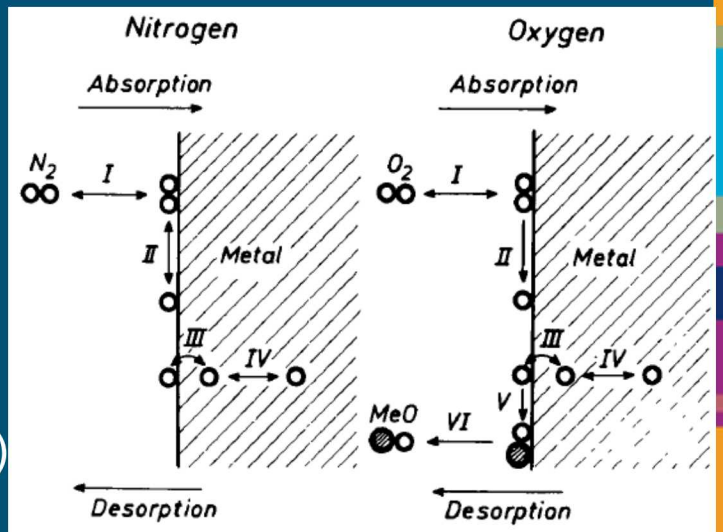


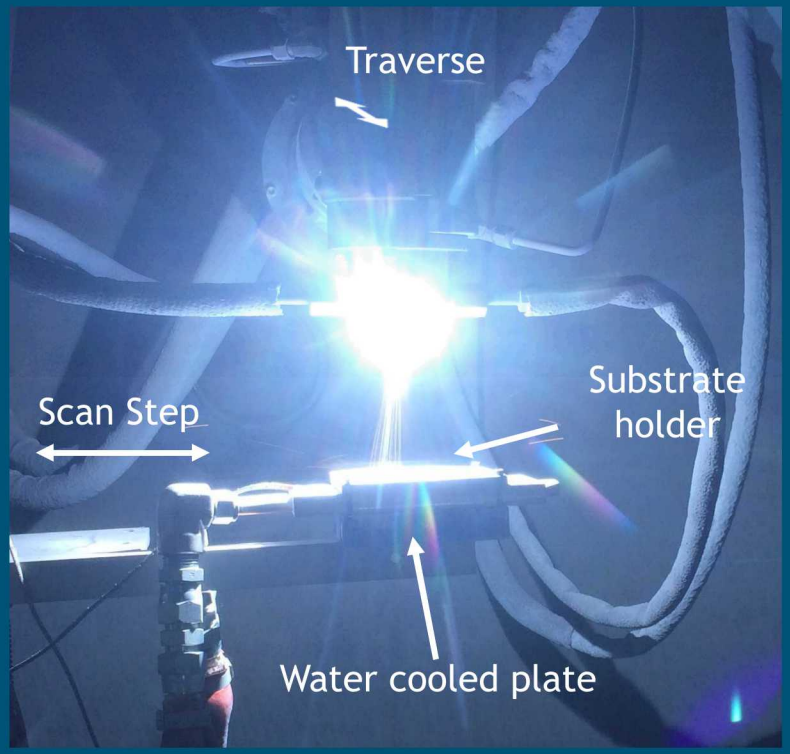
Fig. 1—Mechanisms of absorption and desorption of nitrogen (left side) and oxygen (right side) for VA and VIA metals (schematically).

Hörz, Gerhard. "Mechanisms and kinetics of absorption and desorption reactions in systems of refractory metals with nitrogen, oxygen or carbon." *Metallurgical Transactions* 3.12 (1972): 3069-3076.

Kohl, Walter Heinrich. "Handbook of materials and techniques for vacuum devices." (1967).

CAPS Experimental Parameters

- OC3A Torch (Oerlikon-Metco) with Sandia National Lab's CAPS chamber
  - 102mm and 203mm stand off
  - Ambient air (~630 Torr)
  - Nitrogen, Argon backfill (~460-500 Torr)
- Material sprayed onto Al coupons on water-cooled plate for X-Ray diffraction and metallography
- Aluminum dissolved to produce free-standing deposits for chemical analysis via high-temperature furnace combustion*
  - 80wt% Phosphoric Acid, 5wt% Acetic Acid, 5wt% Nitric Acid
  - DI water wash

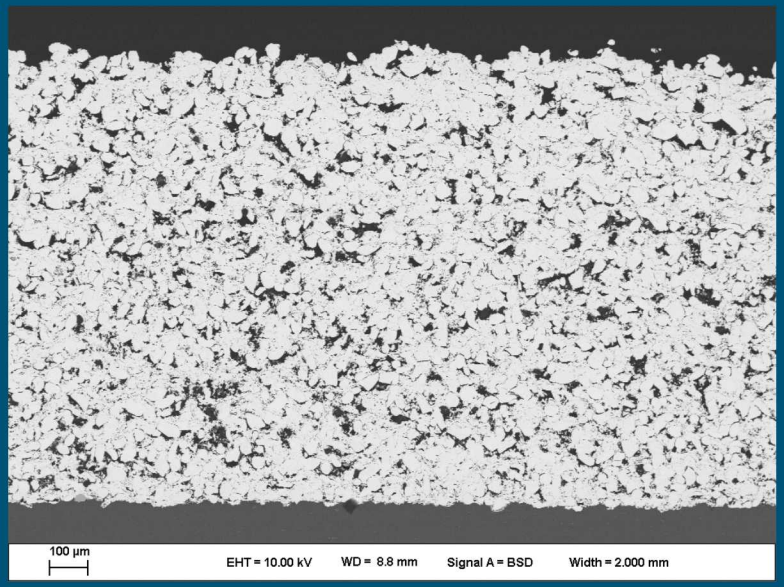


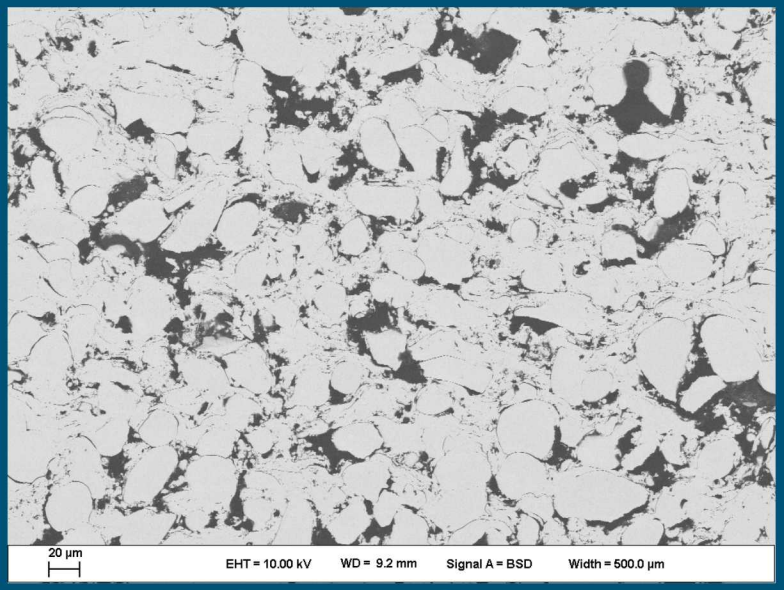
Parameter	Setting
Anode	#93
Cathode	#9
Argon Flow [slpm]	120
Helium Flow [slpm]	15
Current [Amps]	1500
Traverse Speed [mm/s]	50
Scan step [mm]	10

*Performed by ALS Global, Tuscon AZ

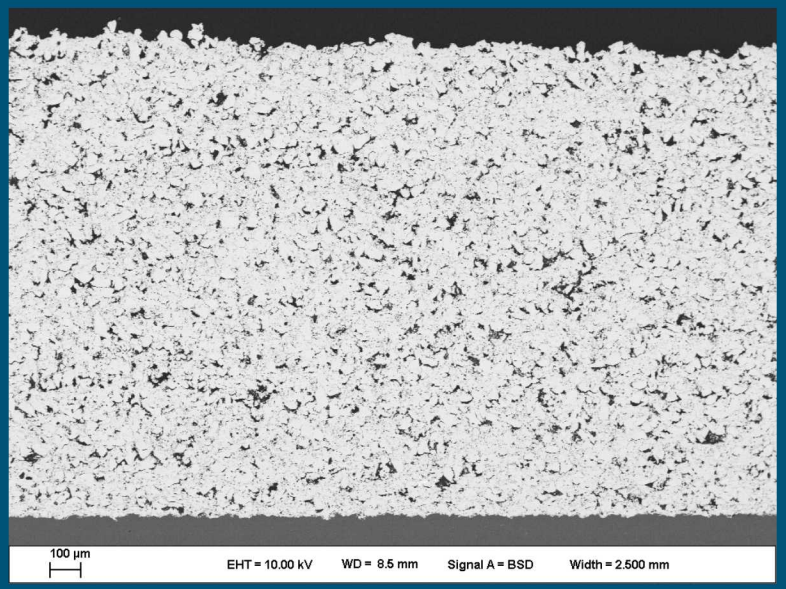
Micrographs of Tantalum and Niobium deposits

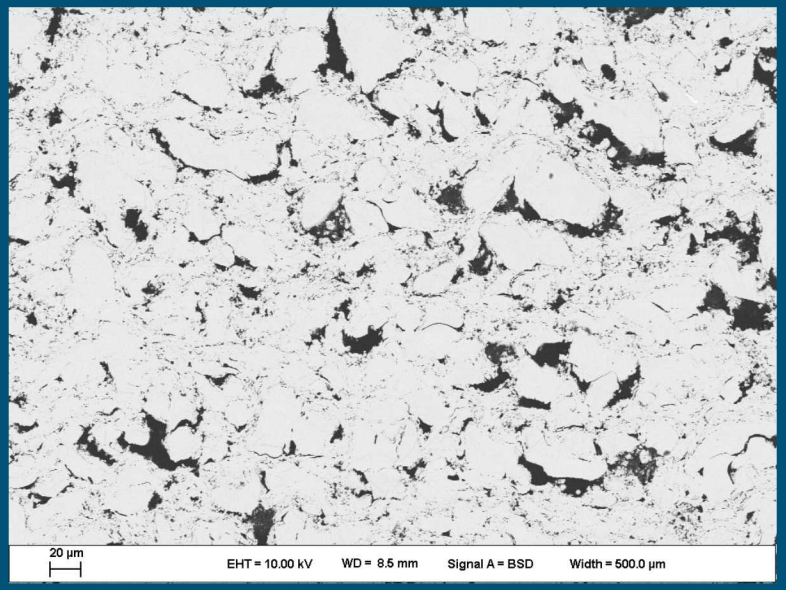
Tantalum





Niobium



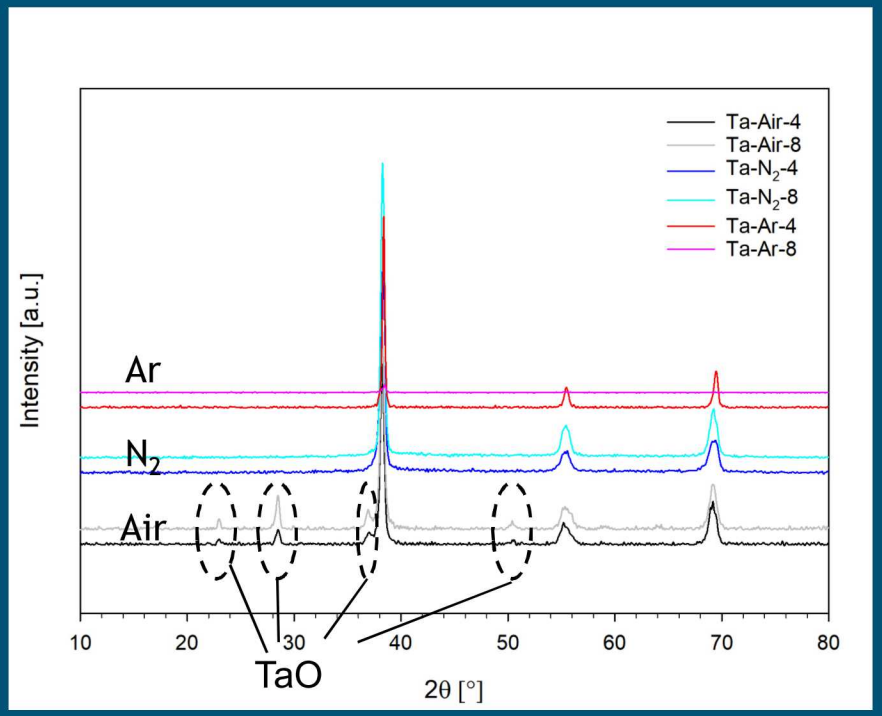


SEM Performed by Sara Dickens, SNL

X-Ray Diffraction of Tantalum and Niobium deposits

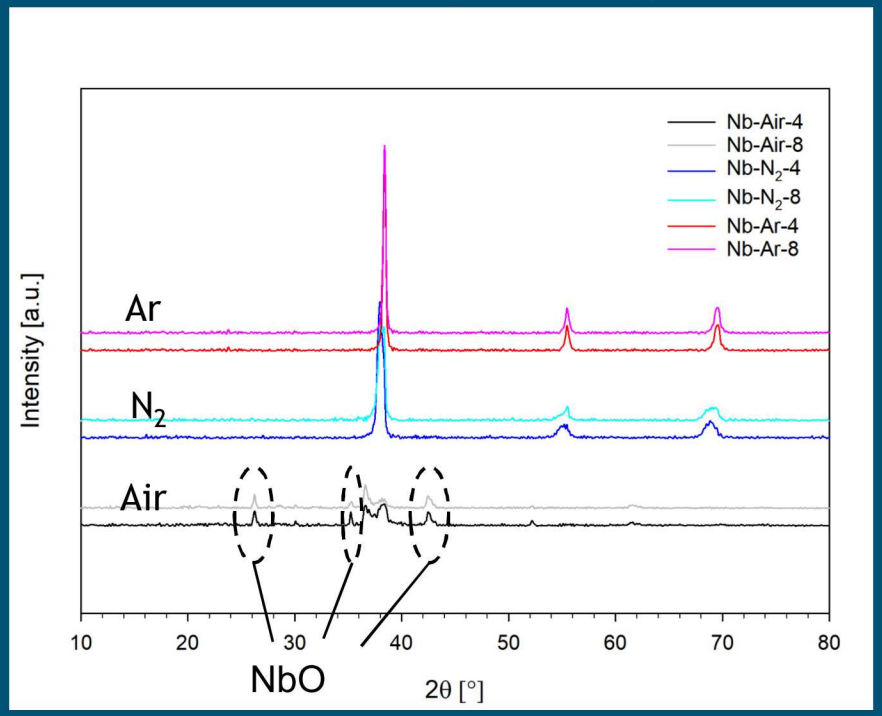
Tantalum

- Significant TaO peaks observed when sprayed in air environment
- No additional or shifted peaks observed when sprayed in Argon or Nitrogen atmosphere



Niobium

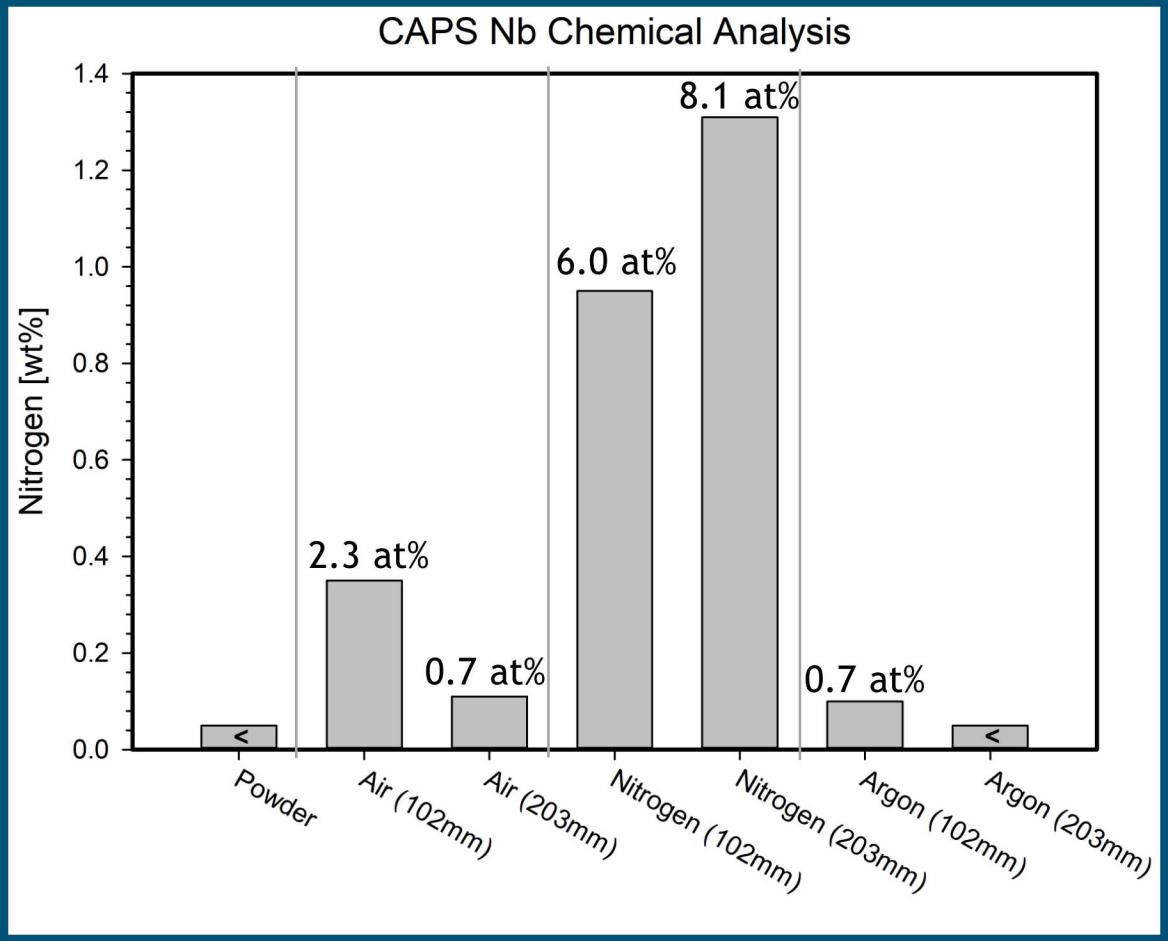
- Significant NbO peaks observed when sprayed in air environment
- Nb peak shift when sprayed in Nitrogen, no additional peaks
- No additional or shifted peaks observed when sprayed in Argon



Chemical Analysis of Samples – Nitrogen

Niobium

- Below detection limit in feedstock powder
- Significant uptake in Nitrogen environment, increasing with longer stand-off
- Decrease in N uptake with longer stand-off in Air
- Nitrogen uptake in Argon environment
  - Possible leak in chamber?

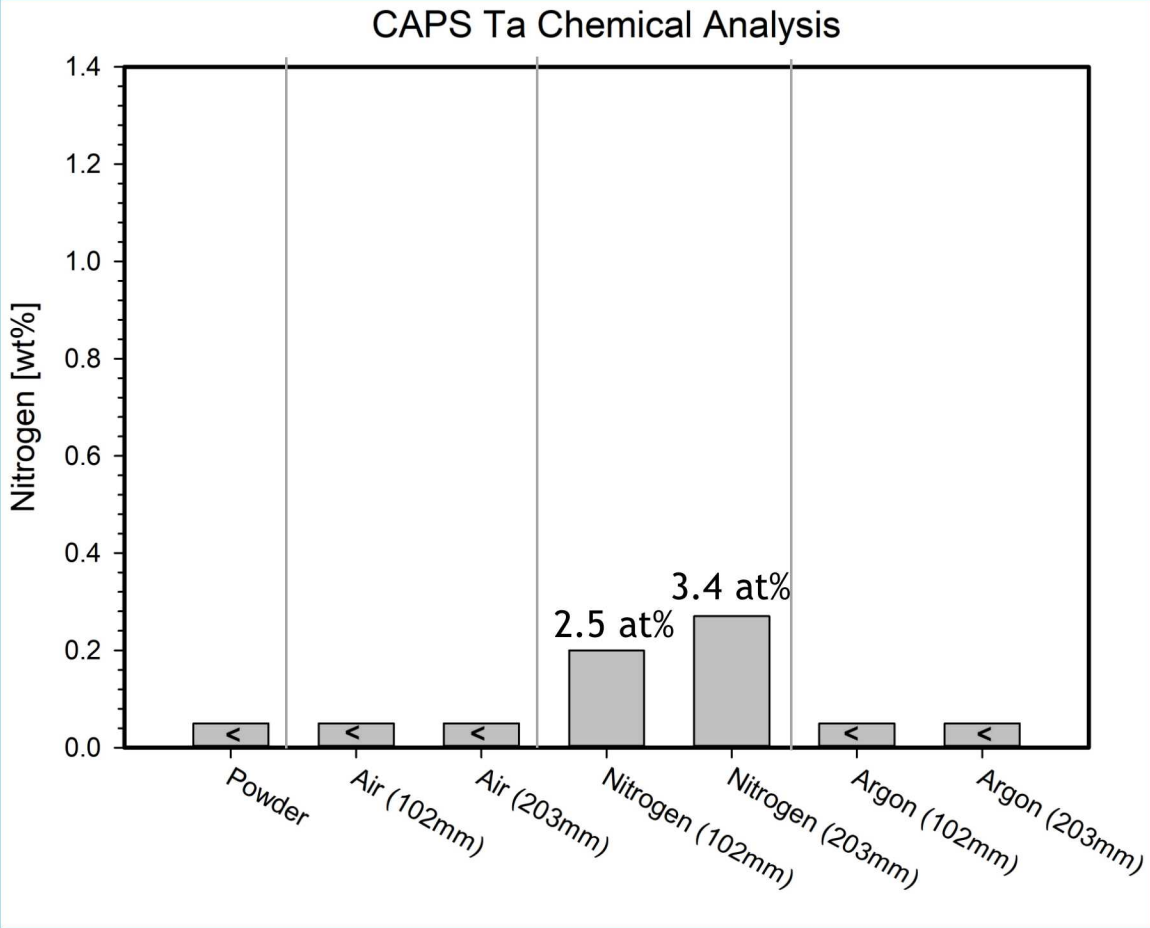


Unable to directly measure Oxygen via high-temperature furnace combustion

Chemical Analysis of Samples – Nitrogen

Tantalum

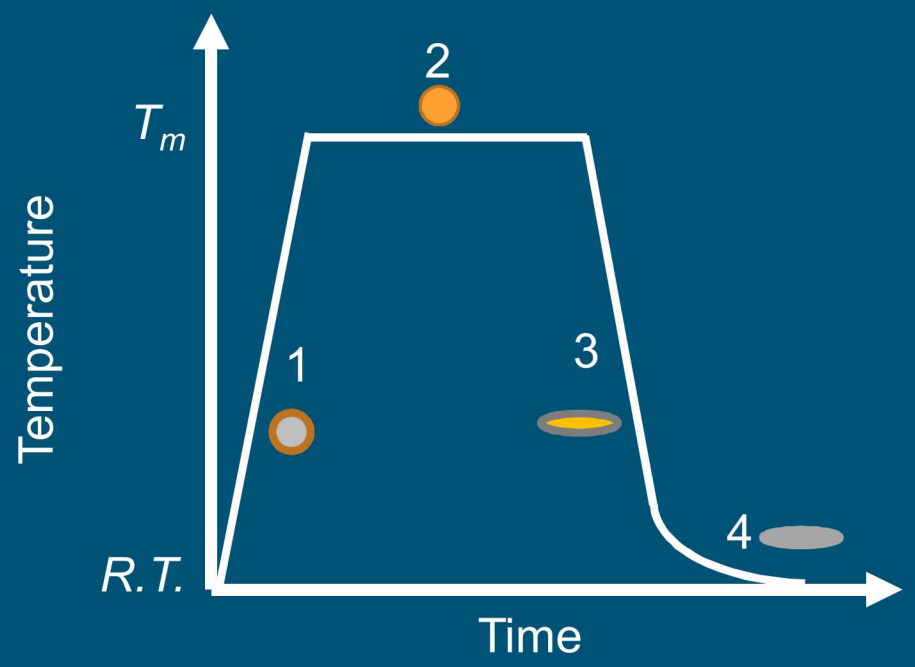
- Below detection limit in feedstock powder
- Significant uptake in Nitrogen environment, increasing with longer stand-off
- No measured Nitrogen uptake in Air and Argon environment



Unable to directly measure Oxygen via high-temperature furnace combustion

Splat Temperature and Time Experience

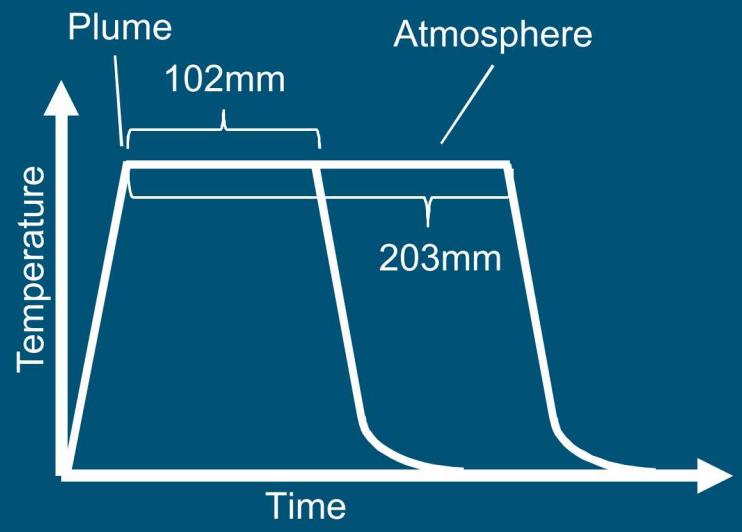
1. Rapid heating and melting in a predominately Ar and He environment
   - Ta_2O_5, Ta_2N, Nb_2O_5, Nb_2N decompose/melt at lower temperatures than their metals
2. Molten in-flight particles, mixing with spray atmosphere
   - On the order of 0.5-1 ms
   - Essentially no solubility limit
3. Rapid quenching and solidification in spray atmosphere
4. Cooled to temperature at or slightly above R.T. in spray atmosphere
   - Temperature and time period are variable, may allow reactions and/or precipitation

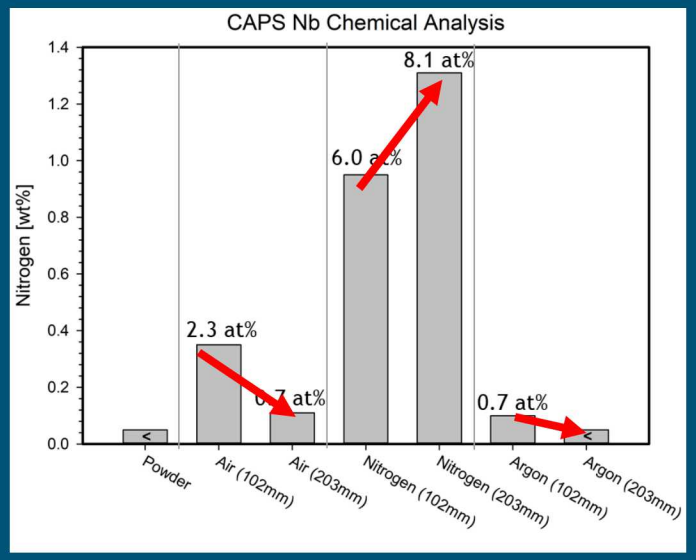


When does O, N uptake and subsequent reactions occur?

Atmosphere Effects

- Longer spray distances shows *increase* in measured Nitrogen when sprayed in Nitrogen atmosphere
  - Longer time of flight for N absorption
- Longer spray distance shows *decrease* in measured Nitrogen when sprayed in Air atmosphere
  - Longer time of flight for O, N absorption
  - Competition between O and N absorption?
  - No direct O measurement, but XRD peaks are present indicating larger volume fraction than N-compounds
- Measured N in Argon atmosphere points to leak in system allowing N_2, O_2, to interact
  - Confirmed leak with later Helium leak testing

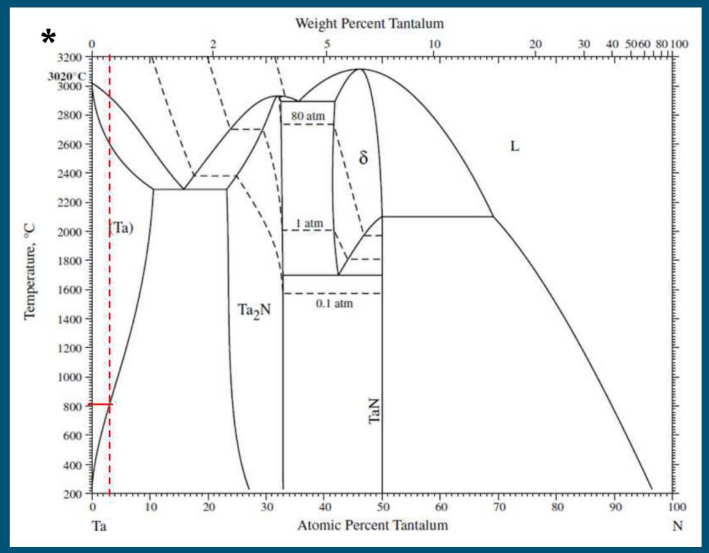


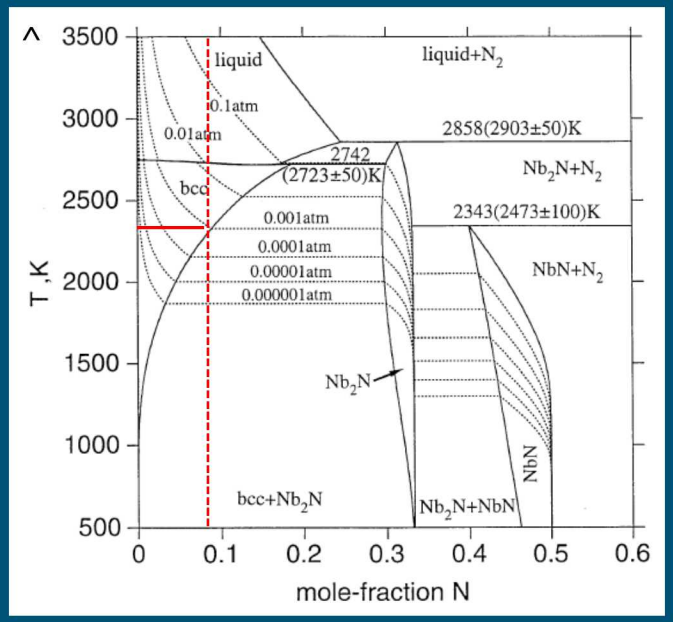


Nitrogen Solubility

- Highest amount measured in Ta samples ~0.3wt% (max 3.4 at%)
  - Precipitation of Nitride expected ~800°C

- Highest amount measured in Nb samples ~1.3wt% (max 8.1 at%)
  - Precipitation of Nitride expected ~2000°C





- Rapid quenching likely suppresses Nitride formation

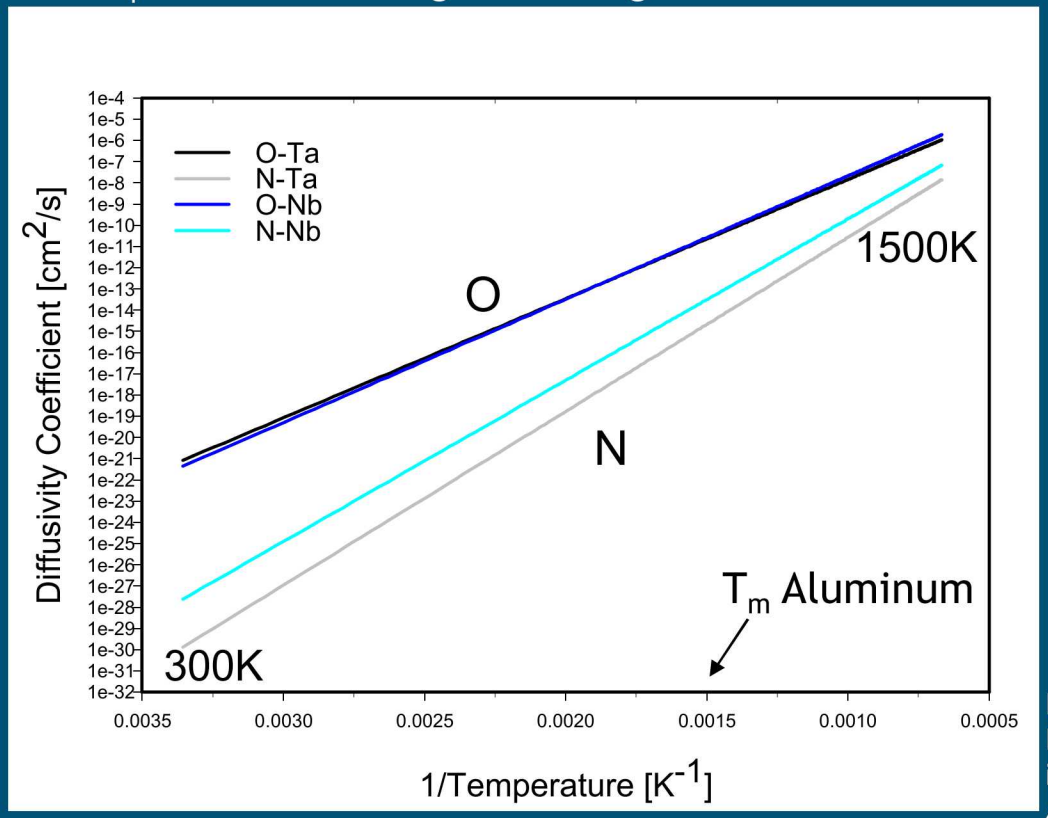
or

- Nitride quantities too low to measure by XRD

*Okamoto, H. "N-Ta (Nitrogen-Tantalum)." *Journal of Phase Equilibria and Diffusion* 29.3 (2008): 291-291.
^Huang, Weiming. "Thermodynamic assessment of the Nb-N system." Metallurgical and Materials Transactions A 27.11 (1996): 3591-3600.

O vs. N Diffusion, Oxide vs Nitride formation

- Re-heating of deposited material may enable diffusion of O, N into Ta or Nb
  - Diffusivity of O > N
- May drive precipitation of Oxides or Nitrides from super saturated deposit
  - ΔH_f an order of magnitude larger for oxide formation



Compound	ΔH°_f [kcal/mol]
Ta_2O_5	-488 ± 0.5*
TaN	-60.0 ±0.6‡
Nb_2O_5	-455.2 ± 0.6*
NbN	-56.8 ± 0.4‡

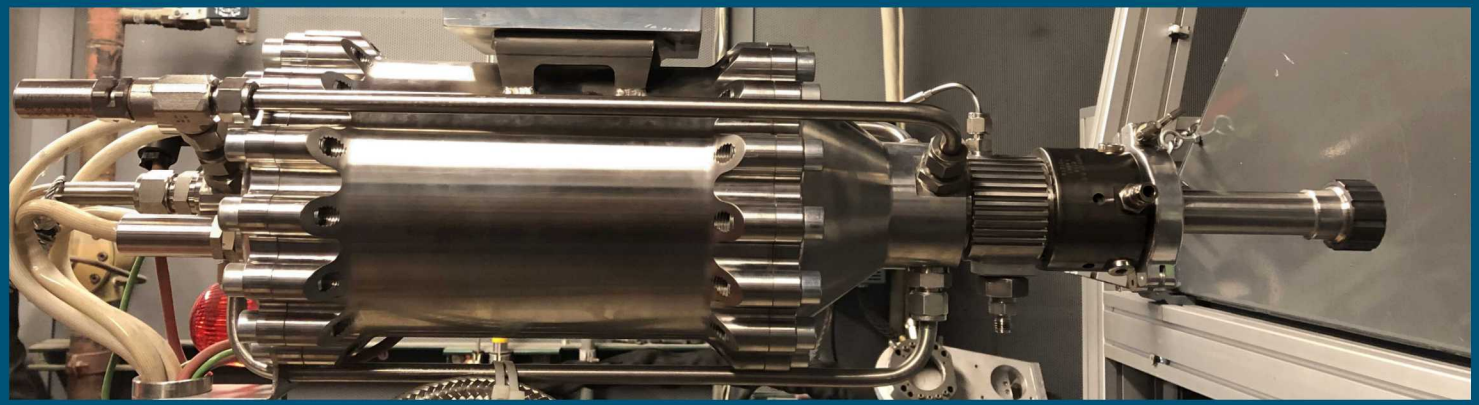
*Humphrey, George L. "Heats of formation of tantalum, niobium and zirconium oxides, and tantalum carbide." *Journal of the American Chemical Society* 76.4 (1954): 978-980.

‡Mah, Alla D., and Norma L. Gellert. "Heats of formation of niobium nitride, tantalum nitride and zirconium nitride from combustion calorimetry." *Journal of the American Chemical Society* 78.14 (1956): 3261-3263.

Derived From:
Powers, R. W., and Margaret V. Doyle. "Diffusion of interstitial solutes in the group V transition metals." *Journal of Applied Physics* 30.4 (1959): 514-524.

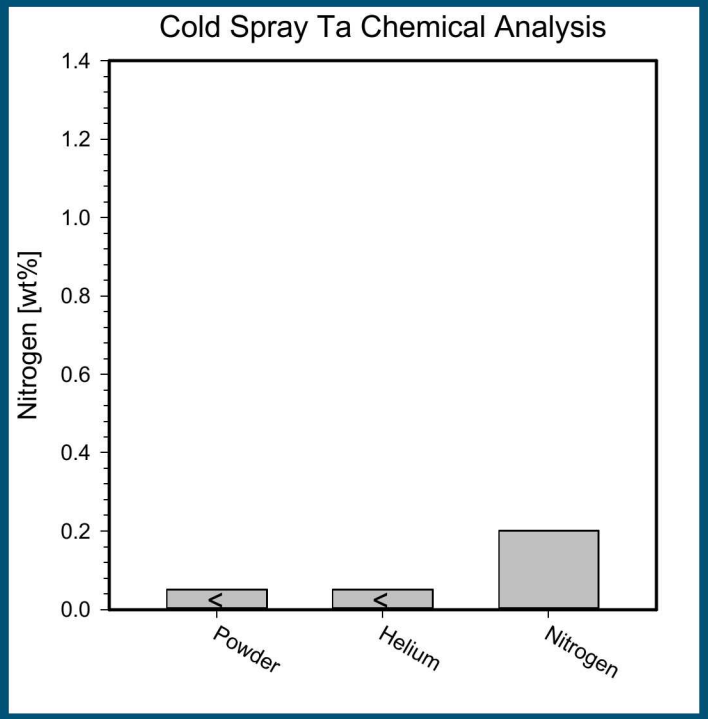
Cold Spray (CS) deposition as an alternative processing method

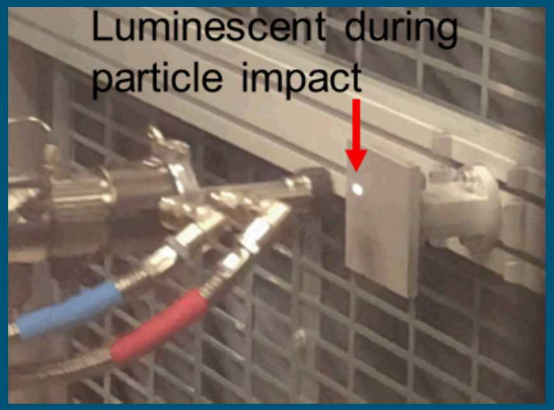
- Cold Spray uses kinetic energy for solid state coating consolidation
  - No melting, lower gas temperatures limits oxidation in commonly CS metals (Cu, Al etc.)
  - Ta and Nb very ductile in a pure state and are readily cold sprayable
- Impact Innovations 5/11 Cold Spray torch
  - Equipped to operate with Nitrogen or Helium carrier gas
  - Coatings able to be made with same feedstock powder as CAPS samples



Chemical uptake in CS processing

- Chemical comparison between samples deposited using Nitrogen and Helium* process gas
- Aluminum dissolved to produce free-standing deposits for chemical analysis via high-temperature furnace combustion**
  - 80wt% Phosphoric Acid, 5wt% Acetic Acid, 5wt% Nitric Acid
  - DI water wash
- Measurable uptake of Nitrogen found in Ta sample
  - Future work to elucidate mechanism





*Sample prepared at New Mexico Institute of Mining and Technology, Socorro NM

**Performed by ALS Global, Tuscon AZ

Conclusions and Future Work

Conclusion

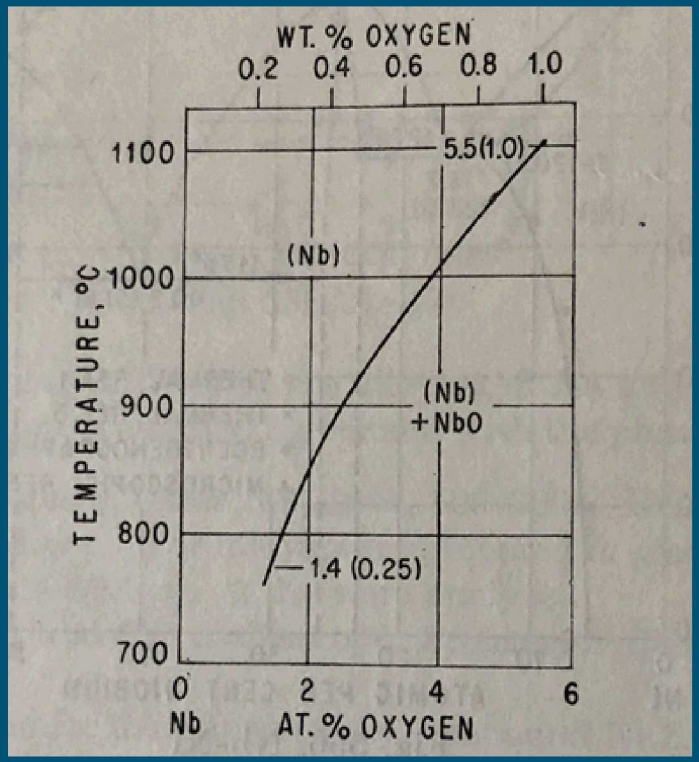
- Controlled atmosphere plasma spraying can reduce oxide formation to levels below XRD detection in Ta an Nb
  - N_2 atmosphere still allows N uptake
  - Ar best atmosphere for future processing of higher purity deposits
- Super-saturation of N within Ta, Nb possible but likely suppressed by rapid splat quenching
- Cold Spraying processing with Nitrogen results in N uptake in Ta, Nb

Future Work

- Reduce leakage of Air into CAPS chamber by spraying a positive pressure Argon atmosphere
  - O, N source from process gas and feedstock impurities
- Switch from LLPS torch to torch commonly used in atmospheric pressure
  - Enhance melting efficiency of powders
- Elucidate mechanism of Nitrogen uptake in CS Ta
- Thermo-Mechanical measurements of deposits
  - Temperature, thermal cycling dependence

Thank you
Questions?

Backups



^Hansen, Max, Kurt Anderko, and H. W. Salzberg. "Constitution of binary alloys." Journal of the Electrochemical Society 105.12 (1958): 260C-261C.