Engineered Metallic Nanostructures Laboratory

Stabilizing Nanocrystalline Grains in Tantalum through Impurity Additions

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Background & Motivation

According to the World Nuclear Association and the International Energy Agency (IEA), the worlds electricity demands will increase by at least 80%. This demand requires new reactors to be built [1].

- Next generation nuclear reactor materials conform to a new set of requirements which focus on improved strength and radiation tolerance, increased lifetimes, and higher operating temperature conditions [2-4].
- New materials are needed to meet these demanding requirements, and nanocrystalline refractory metals, have demonstrated promising results [2]. Tantalum is considered here due to its applicability for extreme temperature environments [5].

The focus of this study was to examine the thermal stability of nanocrystalline Ta thin films synthesized by pulsed laser deposition.

- This research implemented *in situ* transmission electron microscopy (TEM) techniques and molecular dynamic simulations to characterize microstructural evolution during heat treatment of nanocrystalline tantalum thin films [6].
- By quantifying the structural stability of engineered nanocrystalline refractory metals at elevated temperatures, next generation reactor materials can be designed for future evaluation of other critical performance metrics such as radiation tolerance.

Sample Preparation using Pulsed Laser Deposition (PLD)

Nanocrystalline Ta thin films were deposited at Sandia National Laboratories by:

- Nominally 100-150 nm thick Ta films deposited using a KrF excimer laser, $\lambda = 248$ nm onto polished NaCl substrates.
- System employed a raster system to limit the incorporation of impurities.

Experimentation & Analysis of PLD Samples

Nanocrystalline Ta films were analyzed *in situ* through:

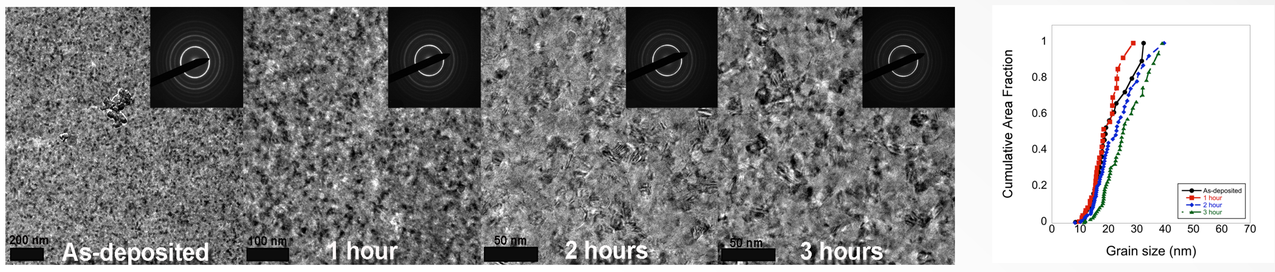
- Annealing in a Philips CM-30 and JEOL JEM 2100F TEM using a Gatan heating holder operating between 800-1200°C.
- Electron energy loss spectroscopy (EELS) was performed using the JEOL JEM 2100F TEM.
- Image analysis was accomplished using ImageJ and Adobe Photoshop. Phases were identified through integrated radial intensity plots.

Molecular Dynamic Simulations

A 10 nm grained columnar nanocrystalline Ta structure was analyzed by:

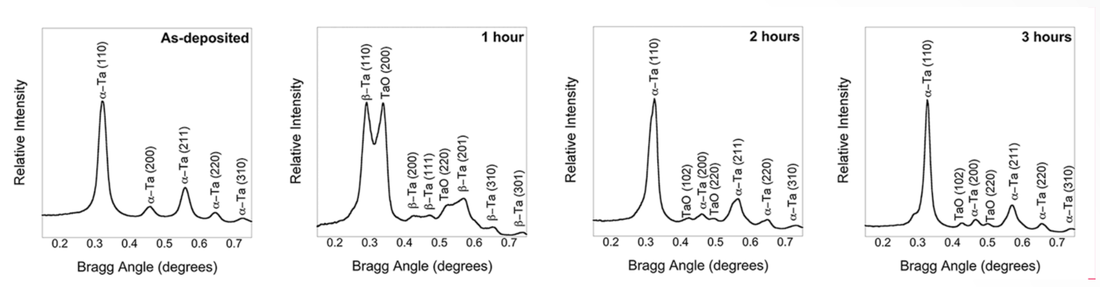
- Simulated 25 ns anneals from 225-1225°C following an energy minimization
- Employed an EAM potential developed by Ravelo et al [7] for Ta

Grain Growth in Nanocrystalline Tantalum Thin Films



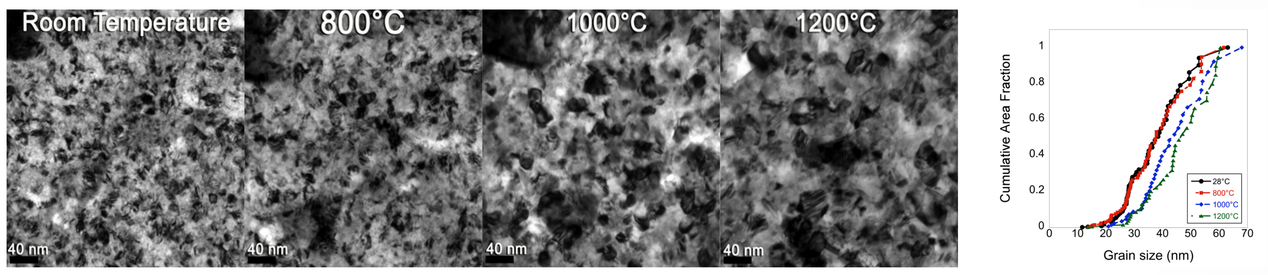
***In situ* isothermal anneals were conducted on the 100 nm-thick film and revealed:**

- Limited grain growth regardless of time with average grain size fluctuating between 17 and 23 nm
- The subtle increase between 2 and 3 hours represented the only quantifiable change beyond measurement error



Quantitative analysis of the produced radial intensity plots illustrated:

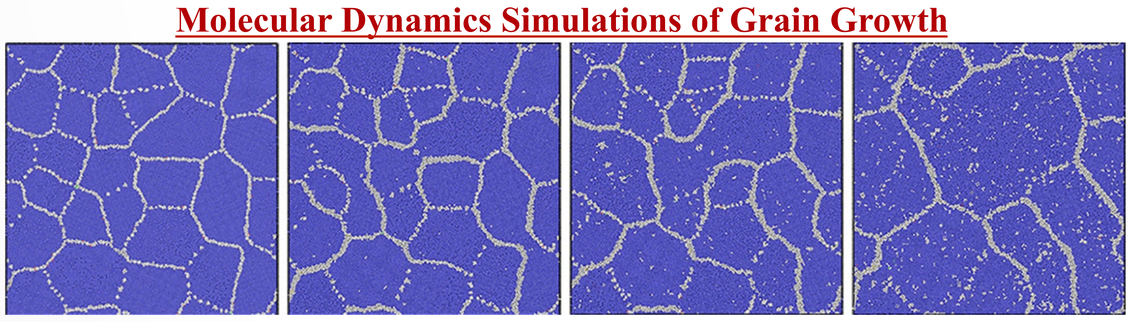
- Initially the film consisted only of the BCC α-Ta phase, which represents the equilibrium metallic phase of Ta.
- Upon annealing at approximately 800°C for 1 hour, an α → β transition was detected and accompanied by the formation of TaO
- The film transformed back to α-Ta after 2 hours of annealing, which was expected since the annealing temperature was near the β → α transition temperature of 755-775°C [8].



***In situ* anneals from room temperature (28°C) to 1200°C of 150 nm thick Ta film demonstrated:**

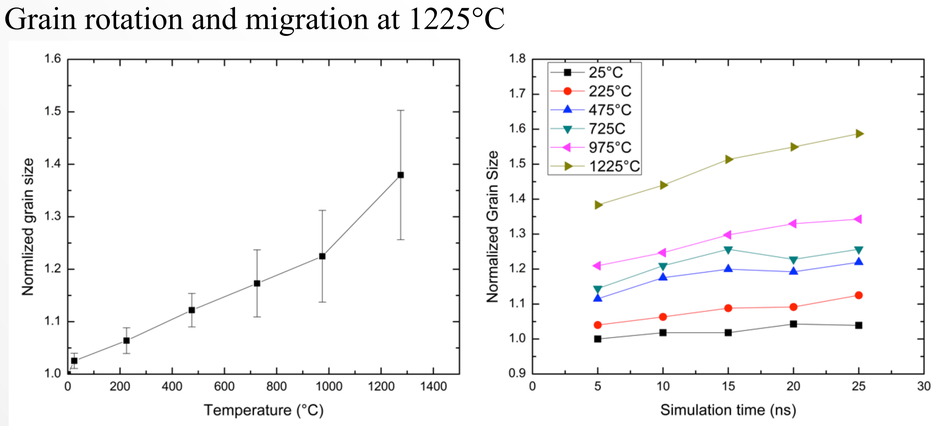
- The absence of grain growth up to 800°C, which represents roughly 25% of Ta's melting point
- Annealing at 1200°C (40% of the melting point) exhibited a 25% increase in grain size, which represents unusually high thermal stability for an elemental nanocrystalline metal

Molecular Dynamics Simulations of Grain Growth



Grain evolution was determined to be caused by:

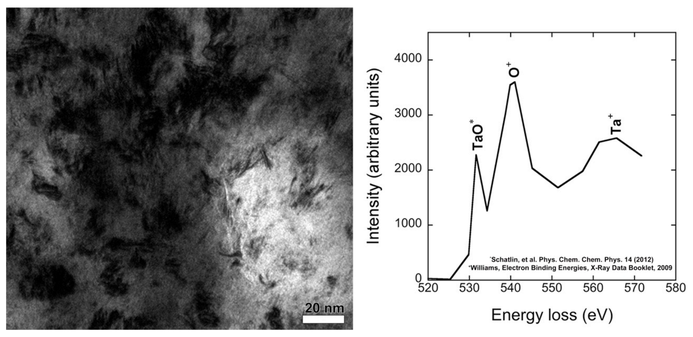
- Instabilities in the high angle boundaries at 725°C
- Boundary annihilation through grain migration at 975°C
- Grain rotation and migration at 1225°C



Nanocrystalline Ta demonstrated more extensive grain growth

- A 52% increase in grain size is observed
- Perpetual increase in grain size throughout is indicative of structural instabilities

Stabilization through Impurity Addition



Impurity content of a 26 nm thick Ta film was analyzed using EELS and showed:

- Oxygen impurities were confirmed to be present in the as-deposited films
- EELS peaks were attributed to TaO, O and Ta and suggests the as-deposited films contained oxygen in solid solution as well as a thin surface oxide layer prior to annealing
- Stabilization of "pure" nanocrystalline films has been attributed to oxygen enrichment at grain boundaries in Al [9].

Conclusions

Exceptional thermal stability was observed in nanocrystalline tantalum thin films:

- Virtually no grain growth observed at temperatures up to 800°C (representing 25% of Ta's melting pt)
- Annealing of nanocrystalline tantalum films at temperatures up 1200°C produced only modest evolution of the microstructure with nanocrystalline stability at 40 nm.

MD Simulations demonstrated:

- A dramatic increase in grain size up to 1225°C, confirming the unusual stability of the Ta films

Stabilization of the film attributed to:

- The presence of oxygen impurities in the as-deposited films, which acted to stabilize the nanostructure as confirmed by electron diffraction analysis and EELS.

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