

High-Temperature Hydrogen Effects on Oxide Stability and Surface Evolution in Refractory Metals

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INTRODUCTION

Hydrogen is an emerging clean energy carrier for next-generation power systems. Hydrogen turbines operate at extremely high temperatures (>1200 °C), requiring materials that maintain strength, resist oxidation, and remain stable under thermal stress. Refractory metals such as niobium (Nb) and tantalum (Ta) are promising candidates due to their high melting points and thermal stability. However, exposure to hydrogen can reduce protective oxide layers and change surface chemistry, which may affect friction and wear behavior. Despite their importance, the temperature thresholds for oxide reduction and the relationship between hydrogen-induced surface changes and tribological performance remain poorly understood. This study investigates how hydrogen exposure alters oxide stability and surface chemistry in refractory metals.

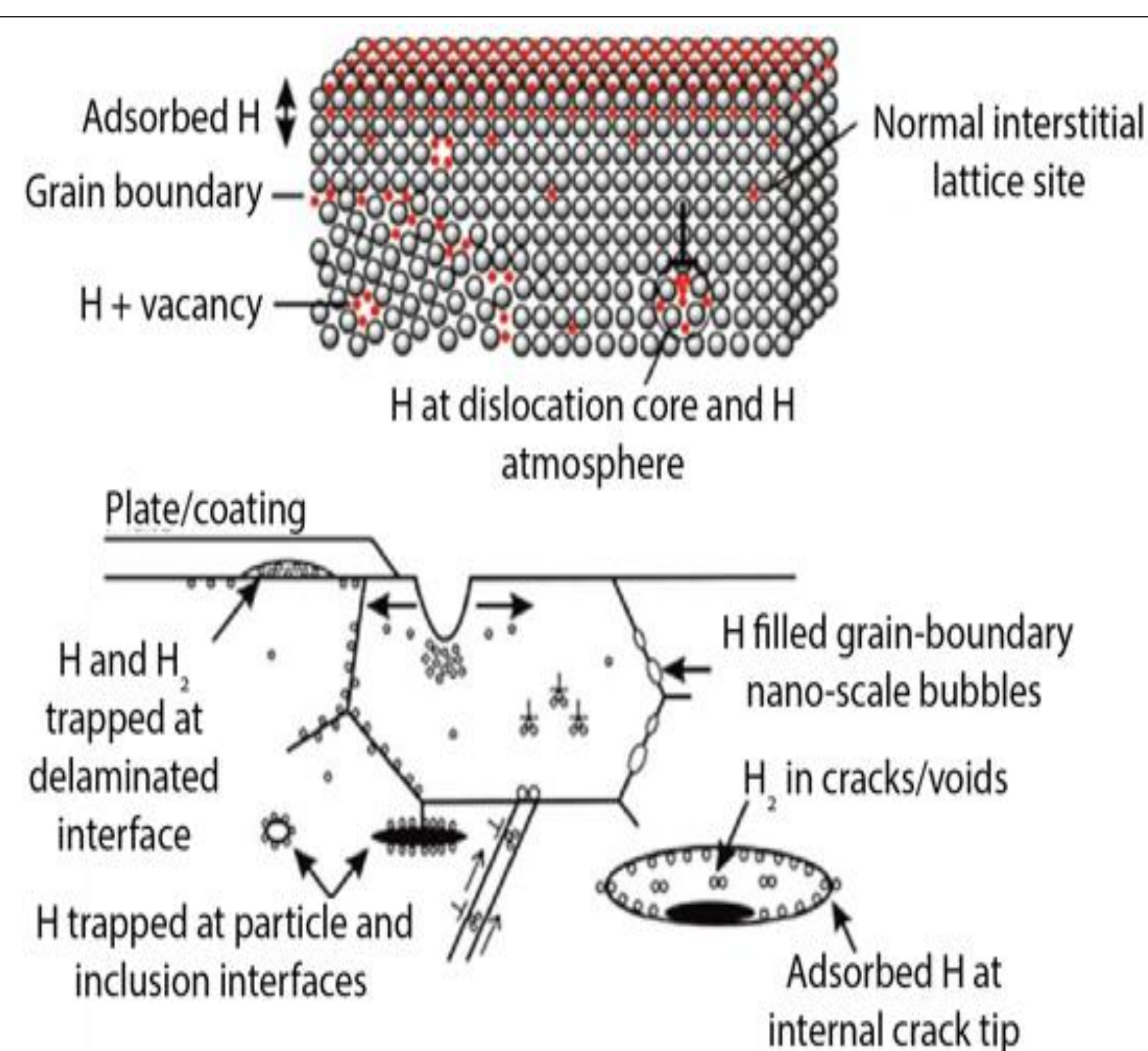


Fig 1. Hydrogen Trapping in metals

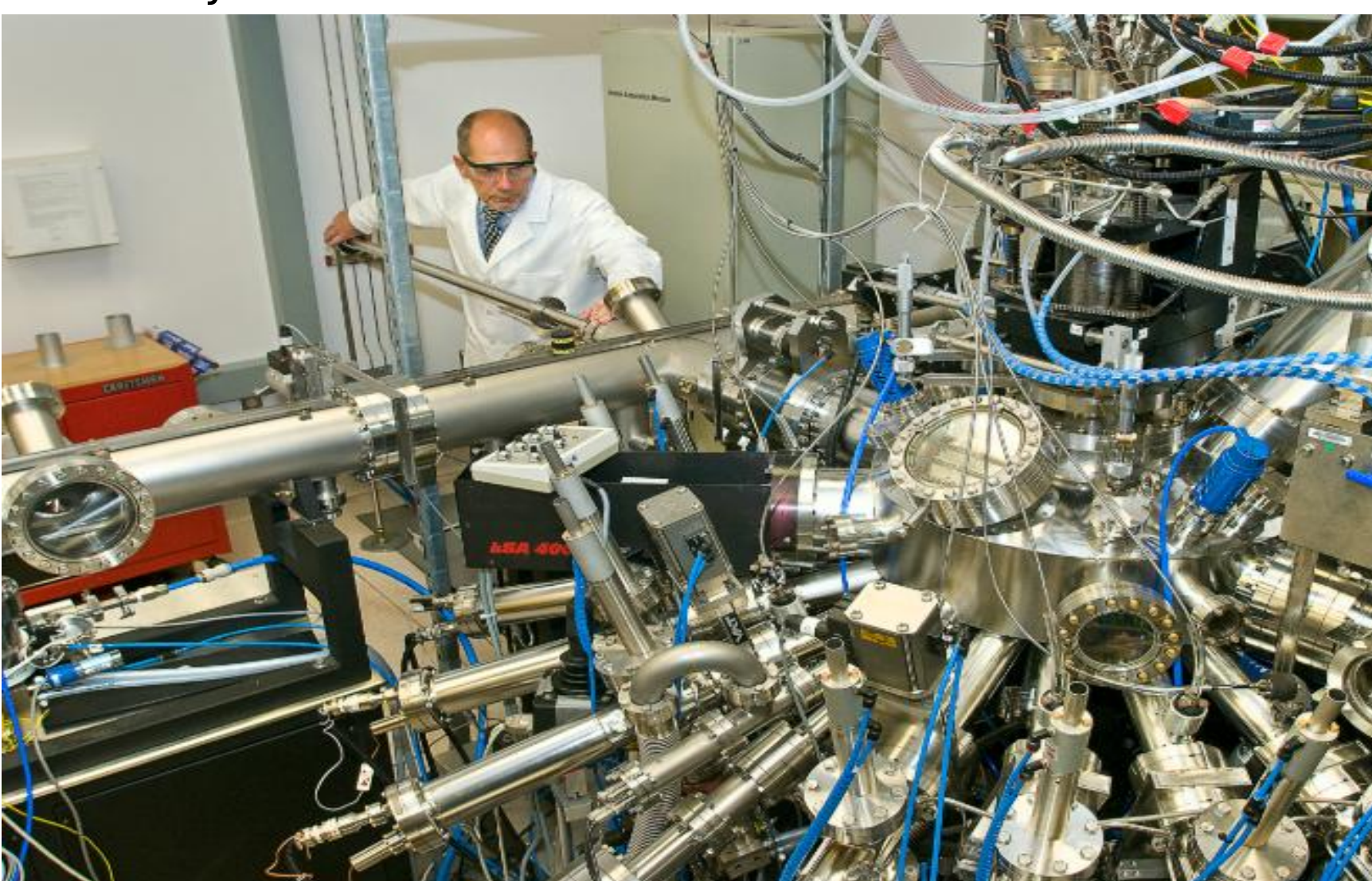


Fig 2. Ambient pressure XPS system

Fig 3. Materials being aged in hydrogen



Fig 4. Hydrogen furnace



MATERIALS AND METHODS

- Refractory metal samples with native oxide layers
- High-temperature hydrogen furnace capable of controlled atmosphere exposure
- Ultra-high purity hydrogen gas supply
- Tribometer for controlled friction and wear testing
- X-ray Photoelectron Spectroscopy (XPS) system for surface chemical analysis
- X-ray Diffraction (XRD) instrument for phase identification
- Electron microscopy equipment for microstructural observation

(XPS) X-RAY PHOTOELECTRON SPECTROSCOPY

- X-ray Photoelectron Spectroscopy (XPS) performed after hydrogen exposure
- Spectral comparison and peak deconvolution
- Analysis of peak position and intensity changes
- Identification of oxide decomposition temperature
- Correlation of chemical changes with phase evolution

HYDROGEN EXPOSURE

- Samples placed in a controlled high-temperature furnace
- Hydrogen atmosphere at ~1 bar pressure
- Flow rate: ~1 L/min
- Temperature range: 296 K to 923 K (23 °C to 650 °C)
- Stepwise temperature ramp across multiple temperature conditions
- Objective: identify oxide decomposition thresholds

RESULTS

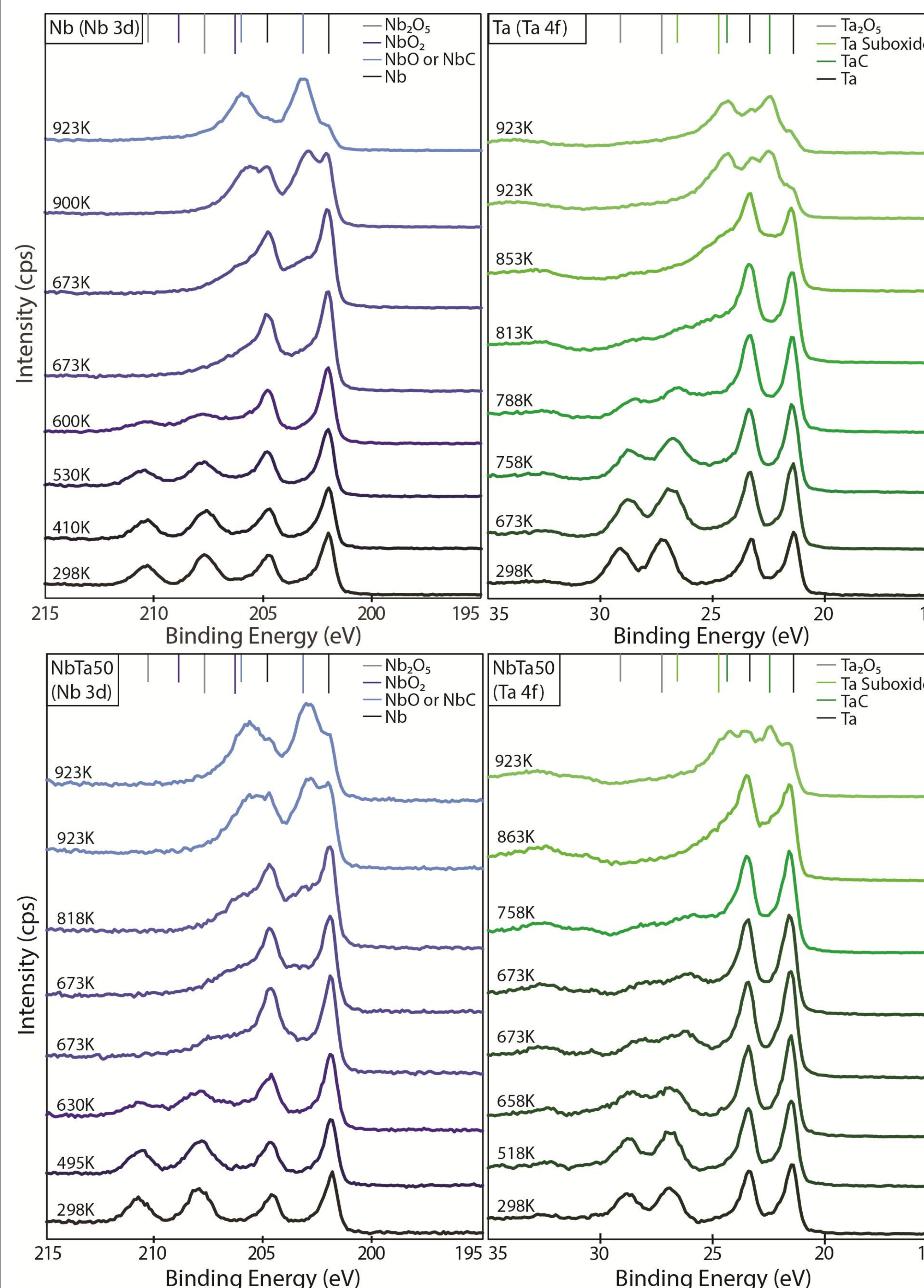


Fig 5 . X-ray Photoelectron Spectroscopy (XPS) peaks

NIONIUM (Nb)

- At 296–473 K, surface dominated by Nb₂O₅ and metallic Nb (stable native oxide).
- Between ~530–673 K, Nb₂O₅ decreases significantly while NbO and metallic Nb increase → onset of hydrogen-induced oxide reduction.
- Around 673 K, Nb₂O₅ is nearly eliminated, indicating major oxide decomposition.
- Above ~900 K, NbC formation becomes significant → carbide formation after oxide removal.

TANTALUM (Ta)

- At 296–473 K, surface dominated by Ta₂O₅ and metallic Ta (stable native oxide).
- Between ~530–673 K, gradual decrease in Ta₂O₅ observed, but oxide remains largely stable compared to Nb.
- Oxide reduction occurs at higher temperatures than Nb, indicating greater hydrogen resistance.
- At elevated temperatures (≥ ~900 K), increased metallic Ta signal suggests progressive oxide decomposition.

RESULTS CONTINUED

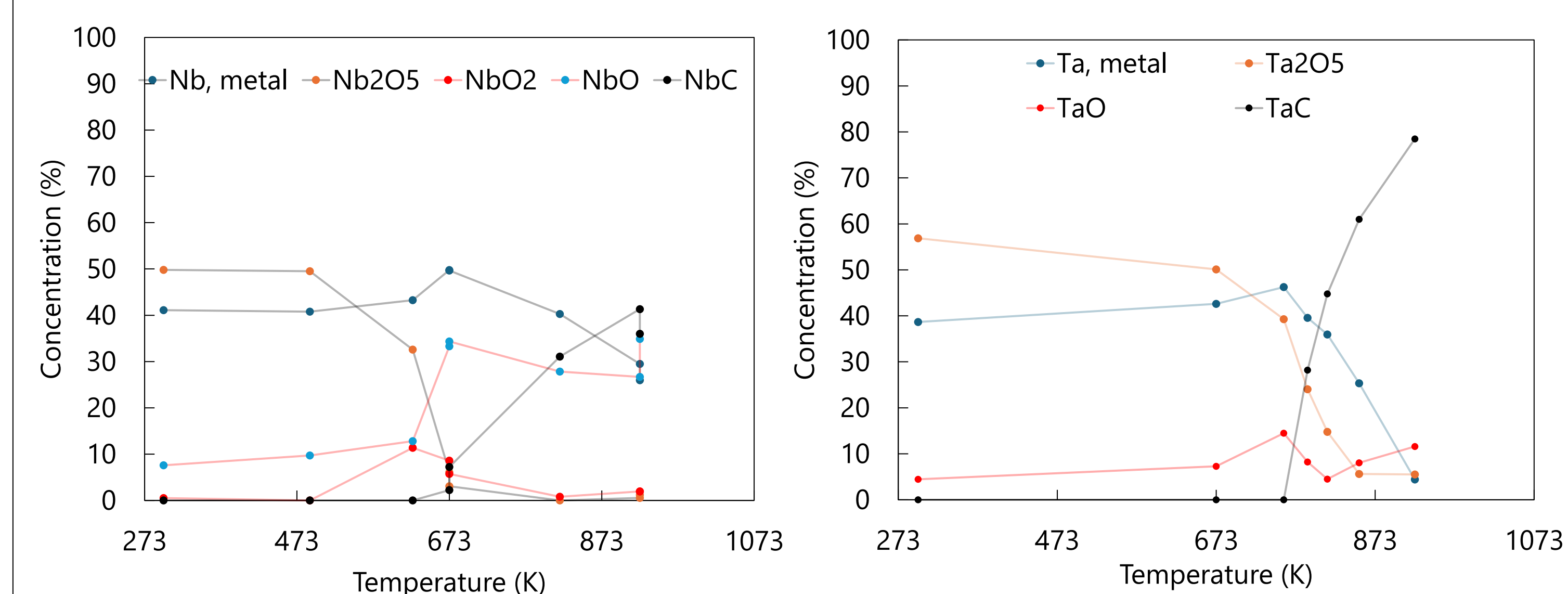
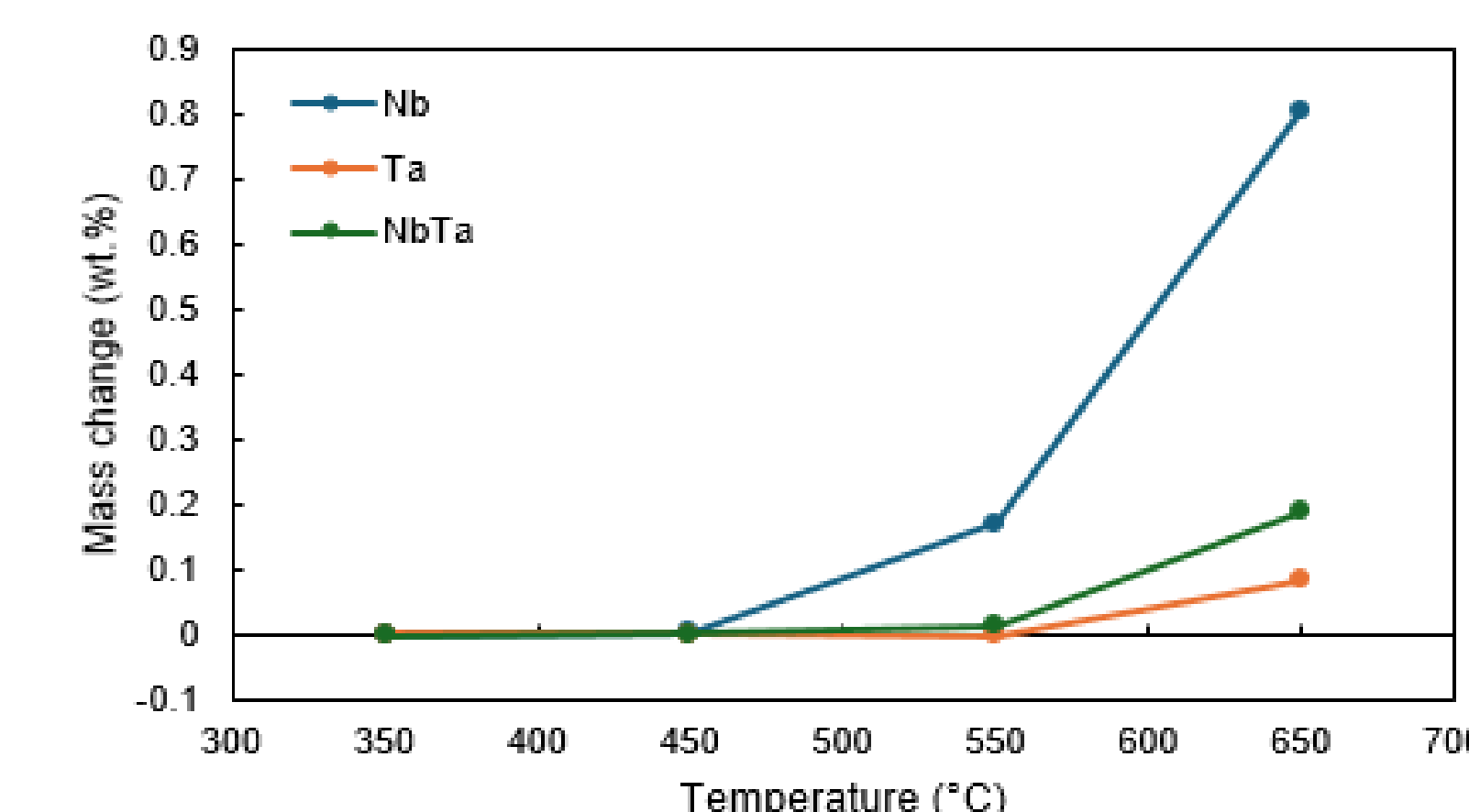


Fig 6 . NIONIUM (Nb)

Fig 7. TANTALUM (Ta)

- X-ray Photoelectron Spectroscopy (XPS) spectra show measurable surface chemistry changes after hydrogen exposure.
- Oxide peak intensities decrease at elevated temperatures, suggesting partial oxide decomposition.
- For Nb, the intensity of Nb₂O₅ decreases significantly between 550–650 °C, while metallic Nb and NbO peaks increase, indicating oxide reduction at elevated temperature.
- Ta₂O₅ remains more stable over the same temperature range, showing smaller changes in oxide intensity compared to Nb.
- Mass change measurements show negligible variation at 350 °C and 450 °C for all materials.
- At 550 °C, Nb begins to show measurable mass increase (~0.17%), while Ta and NbTa remain near zero.
- At 650 °C, Nb exhibits a significant mass increase (~0.80%), whereas NbTa shows moderate uptake (~0.19%) and Ta shows limited uptake (~0.08%).
- The temperature at which Nb mass increases corresponds to the temperature range where oxide reduction is observed by XPS.

Fig 8. Mass uptake fig



ONGOING/ FUTURE WORK

- Determine the full temperature range for oxide decomposition in hydrogen.
- Measure carbide formation rates at higher temperatures.
- Confirm phases using X-ray diffraction (XRD).
- Study microstructure using scanning electron microscopy (SEM).
- Correlate chemical changes with friction and wear behavior.
- Test conditions closer to hydrogen turbine environments.
- Extend experiments beyond the current limits (~650 °C and ~1 bar hydrogen pressure).
- Use simulations to model surface reactions and predict material behavior at turbine-relevant conditions.

CONCLUSIONS

- High-temperature hydrogen exposure reduces the native oxide layers on refractory metals.
- These changes occur in a temperature-dependent manner.
- Temperature-dependent XPS helped identify when oxide reduction begins.
- A comparison between Nb and Ta showed differences in oxide stability.
- A general correlation was observed between oxide reduction and increased hydrogen absorption.
- This relationship suggests that native oxide layers act as diffusion barriers that limit hydrogen ingress.
- As the oxide decomposes at elevated temperatures, exposed metal surfaces allow greater hydrogen interaction and absorption.
- These chemical changes alter the surface composition of the metal.
- The changes may affect mechanical properties and wear behavior in hydrogen turbine environments.
- Simulations will help model oxide reduction, carbide formation, and surface reactions at higher temperatures and pressures.

REFERENCES

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