

# Characterization of Oxidation on Rhenium and its Effects upon Thermal Ionization Mass Spectrometry

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Rhenium metal is commonly utilized as the ionization filament in the Thermal Ionization Mass Spectrometry (TIMS) for the analyses of uranium and plutonium isotopic ratios in the nuclear forensic and nuclear safeguards community. These filaments are generally prepared by thermal pretreatments to degas and potentially, to carburize the rhenium surface. These processes remove any residual oxidation materials found on the surface. The effect of surface oxidation upon TIMS measurement efficiencies are poorly understood. [1,2] This work is investigating the factors by characterization of the formation kinetics and end species of these formed materials by application of a variety of microanalyses tools.

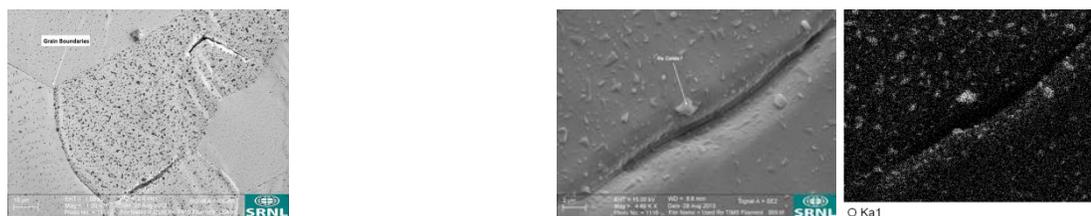
Rhenium employed in TIMS is a high purity ribbon. This material appears to have many different grains under Scanning Electron Microscopy (SEM) analyses, as shown in Figure 1. When examined after thermal pretreatment, and having been stored under ambient conditions, these rhenium metal ribbons undergo surfaces oxidization as observed by the formation of faceted submicron crystalline grains (Figure 1). Analysis of a single crystal by Energy Dispersive Spectrometry (EDS) suggests only the presence of rhenium and oxygen elements. SEM/EDS mapping measurements have shown a clear localization of oxygen on the surface within these crystalline features but suggest that both the densities and sizes of the crystalline materials are not uniform across the metal surface. More specifically, select grains appear to have increased abundance and/or size of these oxidation products compared to other grains. Additionally, there are areas of high concentration of oxidation at many of the grain boundaries.

Characterization of individual crystallites with Raman spectroscopy via Scanning Electron Microscopy Selective Chemical Analyzer (SEM-SCA) demonstrates a spectrum (Figure 2) with a series of intense bands at 967 (s), 916 (m), 893(m), and 333 (s)  $\text{cm}^{-1}$ . Comparison of these bands to reference materials and literature values shows strong agreement with the perrhenate ion (measured as potassium perrhenate), listed in Table 1. The lack of another counter cation in the EDS spectrum suggests that the rhenium oxidation product is either perrhenic acid ( $\text{HReO}_4$ ) or that the cation is rhenium in an additional oxidation state. It should be noted that these materials were observed from two preparation methods after storage under ambient conditions: rhenium ribbon that had been prepared for TIMS use by thermal pretreatment, and rhenium metal plachets which had undergone thermal annealing at 800 °C in an ambient atmosphere. Findings from this work are also consistent with compounds found in other studies which had very different production routes such as rhenium metal oxidization under high pressures in the presence of water [3] or thermal evaporation of  $\text{ReO}_3$  onto quartz substrates [4].

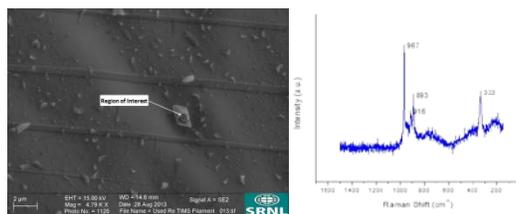
Ongoing efforts will focus on correlation of growth rate of the oxidation product to specific rhenium grain orientation. Electron Backscatter Diffraction (EBSD) will be utilized to map grain orientation of specific regions of a rhenium metal substrate combined with SEM-EDS mapping and Raman spectroscopy. It is anticipated incorporation of the information regarding oxide growth kinetics and products will serve as a basis for better understanding of what the impact of filament oxidation has on TIMS efficiency. [5]

## References

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- [5] The authors would like to acknowledge funding from DE-AC09-08SR22470 and for samples provided by Profs. Jurisson of University of Missouri and Husson of Clemson University.



**Figure 1.** Representative SEM image of a rhenium surface with crystallites (left) and SEM-EDS mapping of a select region showing the localization of oxygen within the crystallite morphology (right).



**Figure 2.** Selected crystallite for in situ Raman spectroscopic showing laser damage post collection of spectra (left) and typical Raman spectrum with four intense bands at 967, 916, 893, and 333  $\text{cm}^{-1}$  (right).

TIMS filament	rhenium planchet	KReO <sub>4</sub> solid	HReO <sub>4</sub> with band assignments [4]
967 (s)	967 (vs)	966 (s)	961 (s) $\nu 1_s$ Re-O
916 (s)	914 (m)	924 (w)	928 (w) $\nu 3_{as}$ Re-O
893 (m)	893 (s)	896 (m)	891 (m) $\nu 3_{as}$ Re-O
			375 (w) $\nu 4$ O-Re-O
	342 (s)	349 (m)	$\nu$ O-Re-O
333 (b/s)	334 (s)	335 (m)	337 (w) $\nu 2$ O-Re-O
	121 (w)		
	106 (w)		

**Table 1.** Table of Raman spectral bands measured in this study compared with literature values for bands and reported vibrational mode assignments for Perrhenic acid.