Oxidation of molybdenum by low energy ion bombardment

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Introduction
In this work, we provide a detailed characterization of room temperature oxidation of Mo from pure Mo metal and CoCrMo alloy by low-energy oxygen ion bombardment using x-ray photoelectron spectroscopy (XPS) and make a comparison with thermal oxidation.

Experimental
All oxidation was done in situ in the main chamber of the XPS instrument. For the ion-beam oxidation we have used a broad beam of 500 eV O$_2^+$ ions with the typical current density of 2 μA/cm$^2$. The thermal oxidation was performed by supplying the pure oxygen gas into the UHV chamber to the pressure of 5 x 10$^{-6}$ Torr.

Cleaned and oxidized Mo surfaces were characterized by our SPECS XPS instrument, equipped with the Phoibos MCD 100 electron analyser and a monochromatized source of Al Ka x-rays of 1486.74 eV.

Oxidation by ion bombardment and thermal oxidation of pure Mo metal

The deconvoluted Mo 3d spectra from a cleaned molybdenum, a sample exposed to 500 eV O$_2^+$ ions for 20 min and after oxidation at RT, with oxygen dose of 5000 L.

Solid lines represent convolution of Gaussians and Lorentzians, while closed circles represent experimental XPS spectrum.

Cleaned samples: Mo and CoCrMo surfaces were first polished with SiC papers of 800–2500 grit and washed in ethanol and distilled water and then additionally cleaned by cycles of low energy Ar$^+$ bombardment at RT.

Oxidation by ion bombardment and thermal oxidation of Mo in CoCrCo alloy

Comparison of Mo 3d core-level XPS spectra from a cleaned CoCrMo surface and surfaces oxidized at RT with 5000 L of oxygen or bombarded with 500 eV O$_2^+$ ions for 20 min (closed circles).

The three fitting doublets of each spectrum (solid lines, representing convolution of Gaussians and Lorentzians) correspond to the emission from MoO$_2$, Mo$_3$O$_7$, and MoO$_3$.

Conclusion
1. The thermal oxidation of Mo in pure Mo metal is not efficient at RT.
2. Mo oxidizes quite easily within the CoCrMo alloy, showing characteristic contributions from the Mo$^{4+}$, Mo$^{5+}$ and Mo$^{6+}$ oxidation states, i.e., MoO$_2$, Mo$_3$O$_7$, and MoO$_3$ respectively.
3. The ion-induced oxidation of Mo is quite efficient at RT in both Mo metal and CoCrMo alloy. Contributions from the Mo$^{4+}$, Mo$^{5+}$ and Mo$^{6+}$ oxidation states are present in all oxidized surfaces with the dominant contribution from the Mo$^{6+}$ states for the high implantation doses of oxygen.
4. The RT ion-induced oxidation of Mo is more efficient than thermal oxidation in both alloy and pure Mo metal samples.

A several Mo 3d spectra taken from a cleaned Mo surface and surfaces bombarded with 500 eV O$_2^+$ ions for two different bombardment times of 5 and 20 minutes.

Mo 3d core-level photoemission spectra from a cleaned molybdenum surface and surfaces after oxidation at room temperature (RT), with oxygen doses of 500 L and 5000 L.

The photoemission spectra taken on the cleaned CoCrMo surface and surfaces oxidized by ion bombardment for two different bombardment times (left) and with two different oxygen doses (right).

SEM image of the CoCrMo surface, taken by our Jeol JSM-7800F microscope, magnified 10000 times and recorded with the gentle electron beam of 0.7 keV.