

Precipitation and surface adsorption of metal complexes during electropolishing. Theory and characterization with X-ray nanotomography and surface tension isotherms

Maryana I. Nave^a, Yu-chen Karen Chen-Wiegart^b, Jun Wang^b and Konstantin G. Kornev^{*a}

^aDepartment of Materials Science and Engineering, Clemson University, Clemson, SC 29634, USA

^bPhoton Sciences Directorate, Brookhaven National Laboratory, Upton, New York 11973, USA

Supporting Information

Composition and thermal analysis

Figure A1 shows the EDS data collected from the white precipitates. From the data shown in the inserted table it can be concluded that the precipitates consist of some oxides or hydrates of tungsten where the potassium is possibly bonded to the tungsten compound or present as a residue in the sample.

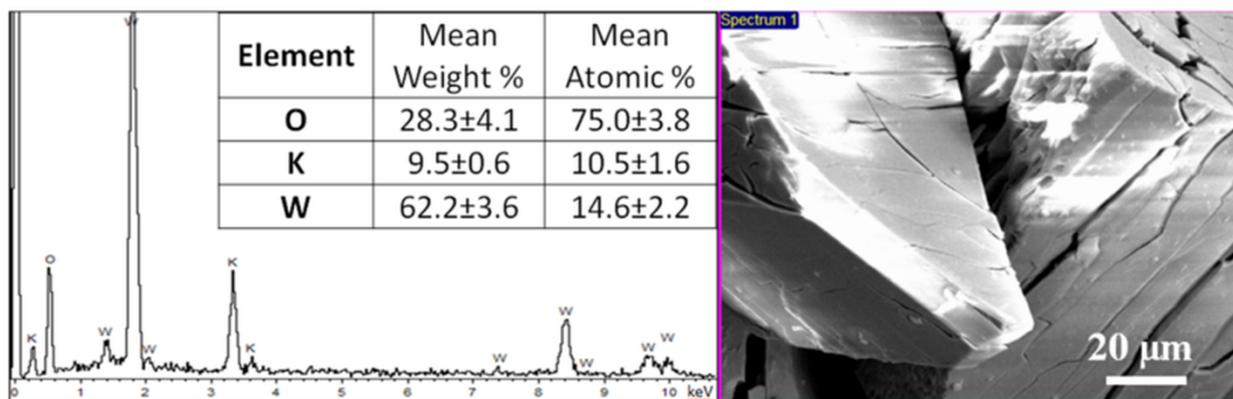


Figure A1. SEM-EDS analysis of the precipitates.

Figure A2 shows the XRD patterns collected from (a) commercial crystalline H_2WO_4 powder that was purchased from Alfa Aesar[®], A Johnson Matthey Company, CAS number 7783-03-1, (b) from the commercial H_2WO_4 powder after the DSC run that was identified as a WO_3 compound, (c) from the white precipitates collected from solution. From Figure A2 (c) it can be seen that the precipitates have an amorphous structure that does not allow determining the composition of the compound using this technique.

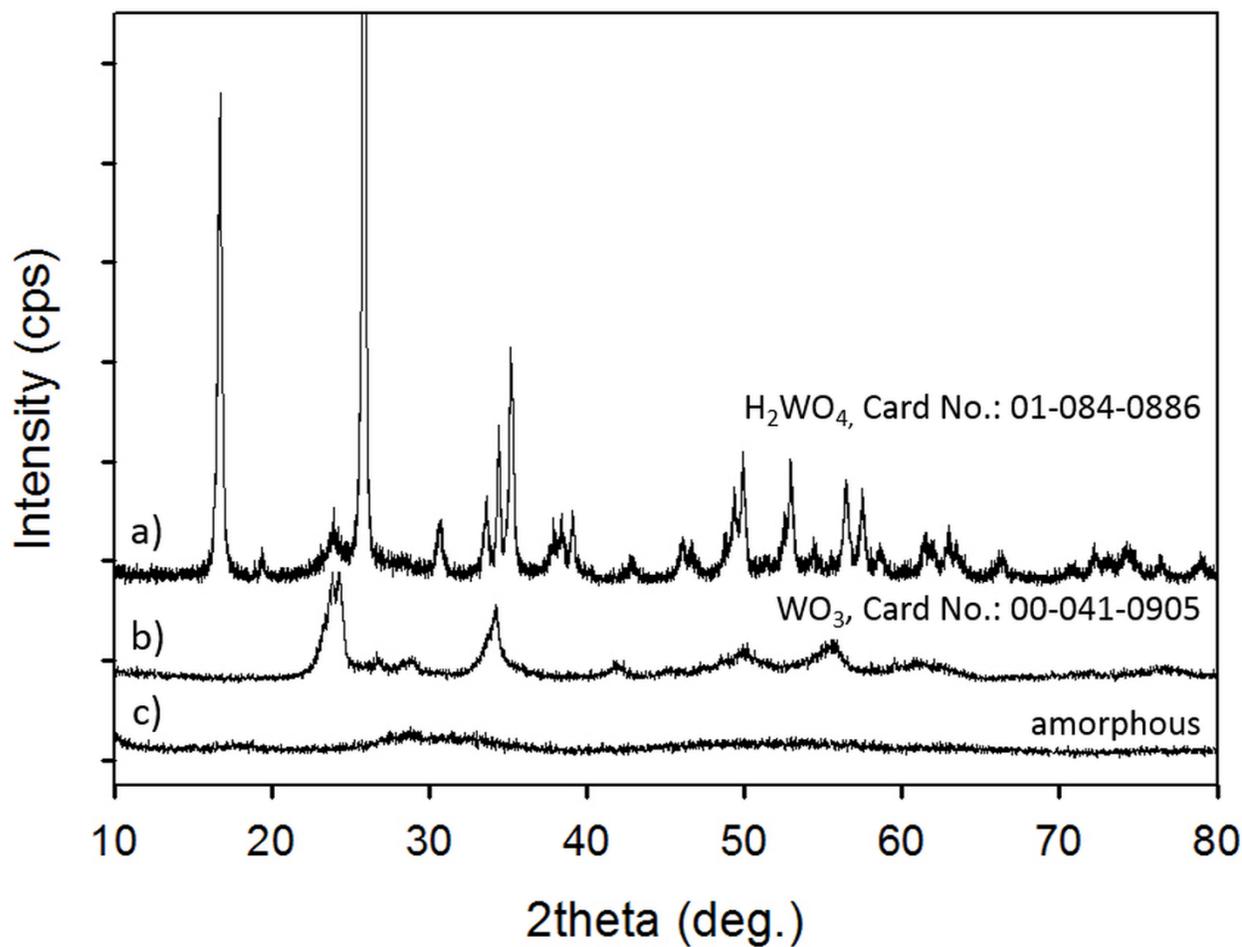


Figure A2. XRD pattern of the (a) commercial H_2WO_4 powder (b) commercial H_2WO_4 powder after DSC run and (c) precipitates from solution (electrolyte after electropolishing the tungsten plate with the CLE technique).

The DSC and TGA curves are shown in Figure A3. From the DSC curve, in our experiment on amorphous samples, it can be seen that there is one endothermic peak at 138°C which is accompanied by the noticeable mass loss of 4.9wt.%. The total mass loss during the heating from the room temperature to 400°C was 7.5wt.%.

The endothermic peaks in the range of 100-300°C temperatures are commonly reported for tungsten and other compounds¹⁻¹³. Figure A3 (b) presents the DSC/TGA curves from the commercial crystalline H_2WO_4 powder. It can be seen that the endothermic peak for the commercial sample occurs at a higher temperature, T=241°C. The total mass loss during the heating from the room temperature to 400°C was 6.8wt.% that correlates with the values from the literature¹¹. In Figure A2 (a) and (b) we show the XRD patterns of the commercial sample before and after the DSC run which show that H_2WO_4 loses its hydrogen and oxygen during the heating process and transforms to WO_3 . A thorough analysis of the crystalline samples of tungsten oxides and hydrates reveals that these compounds undergo phase transitions with the change of the lattice symmetry and release of the volatile oxygen and hydrogen¹⁻¹³. This suggests that the local microstructure of oxides and hydrates undergo a similar change, but the energy required to reorder the lattice constituents can be different because of the lack of crystal order. Therefore, the peak temperature is lower on the amorphous samples.

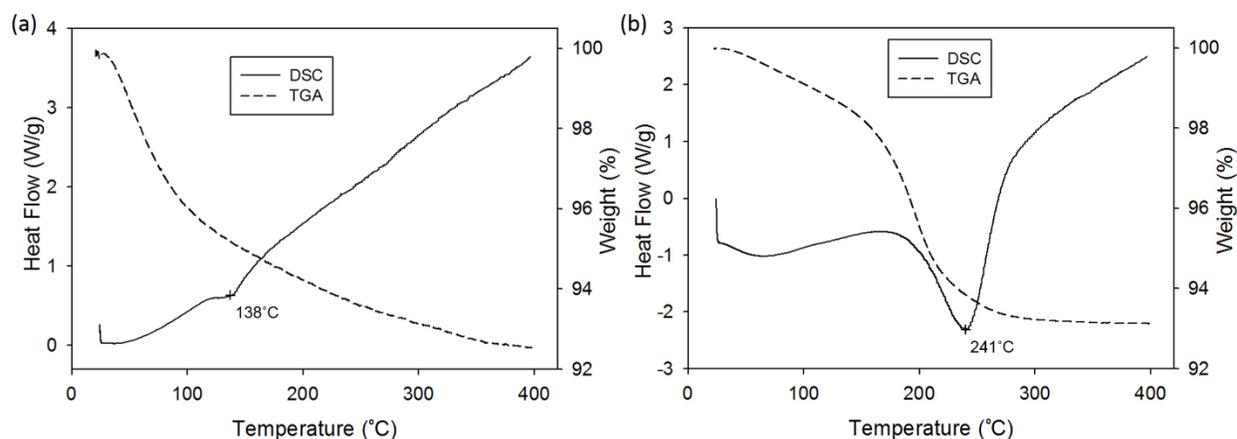


Figure A3. DSC and TGA curves: (a) on the white amorphous precipitates from the electrolyte, and (b) on the commercial crystalline H_2WO_4 sample.

In summary, the results from EDS analysis point to the presence of the tungsten oxides/hydrates in the precipitates, as well as thermal analysis revealed the presence of the structurally bound or hydrated water. This indicates that the precipitates are most likely consisting of tungsten hydrates that are present in the amorphous form.

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