

## Characterization of Spark Plasma Sintered W/VO<sub>2</sub>

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### INTRODUCTION

In order to decrease astronaut exposure to radiation and a weightless environment on deep space missions, it is necessary to develop and alternate means of propulsion to that of chemical propulsion. One option studied by NASA is Nuclear Thermal Propulsion (NTP), whereby, fuel elements fabricated from tungsten/uranium dioxide (W/VO<sub>2</sub>) are considered. These cermet (ceramic/metal) fuel elements must be capable of operating in excess of 2700°K while being compatible with the propellant, typically H<sub>2</sub>. [1] Using W/VO<sub>2</sub> as a fuel element can be used both in power and propulsion at temperatures as high as 3000°K.[2-4] It is not only important to obtain a uniform distribution of VO<sub>2</sub> particles in a tungsten matrix in order to prevent hot spots due to VO<sub>2</sub> segregation, but it is important that the VO<sub>2</sub> remain stoichiometric during operation.

The mechanism for fuel loss of VO<sub>2</sub> depends on where the fuel is located within the cermet.[5] Fuel located on the surface is lost by high temperature vaporization of VO<sub>2</sub> or by diffusion through grain boundaries to the cermet surface. For fuel located within the bulk of the cermet, VO<sub>2</sub> can reduce when heated in an inert, vacuum or hydrogen environment. At temperatures greater than 1400°C, the VO<sub>2</sub> reduces to an oxygen deficient form and free oxygen in the environment in an inert environment and as the temperature decreases, the oxide returns to a stoichiometric state leaving free uranium. Volume changes associated with this mechanism disrupt the cermet and cause mechanical failure. When thermal cycling in a hydrogen environment, hydrogen permeates into the cermet via bulk and grain boundary diffusion through the tungsten matrix. The hydrogen reduces the VO<sub>2</sub> producing oxygen deficient VO<sub>2-x</sub>. Upon cooling, the substoichiometric VO<sub>2-x</sub> disproportionates to free uranium and VO<sub>2-x</sub>. The free uranium, which has a melting point of 1132°C migrates along the grain boundaries of the tungsten matrix and forms UH<sub>3</sub> at ~ 225°C. When UH<sub>3</sub> forms, a large increase in volume can cause stress in the tungsten matrix leading to tungsten grain separation and diffusion of free uranium to the cermet surface. This migration results in not only loss of uranium, but also structural stability of the cermet.

### RESULTS

The purpose of this study was to determine if there was uranium migration during spark plasma sintering and to

determine what crystallographic and chemical changes occurred from this migration.

Four spark plasma sintered specimens from a previous study were chosen for this investigation. [6,7] These specimens were all 60 vol% VO<sub>2</sub>. The following Table gives the sintering temperatures and densities of these samples.

Table I. Sintering Temperature versus Density

Sintering Temperature °C	Density, % Theoretical
1600	97.18
1700	98.19
1750	98.70
1850	99.46

The VO<sub>2</sub> was seen to uniformly distributed within the tungsten matrix. Microstructural and chemical analyses were carried out using transmission electron microscopy (TEM) and atom probe tomography techniques (APT). TEM and APT specimens were prepared at phase boundaries using a lift-out method with a focused ion beam (FIB) instrument. Energy dispersive analysis (EDS) was performed as well. Fig. 1 shows TEM results of a typical sample region of the sample sintered at 1850°C. Based on their diffraction patterns and corresponding EDS results, two phases were identified as tungsten and VO<sub>2</sub>. Fig. 1a is a bright field image taken at a low magnification showing the interface between the tungsten and VO<sub>2</sub>. Fig. 1b is a high resolution TEM (HRTEM) image of the phase boundary. Figs. 1c and 1d are corresponding selected-area diffraction patterns (SAEDP) of the two phases. The dark-contrast of tungsten phase in Fig. 1a means that the orientation of the tungsten phase is parallel to the beam axis. In fig. 1e, the diffraction spots from tungsten and VO<sub>2</sub> overlay one another which means that this phase boundary is coherent. This phase boundary type is typical for all samples except for the one sintered at 1600°C which showed an anomalous third phase, identified as U<sub>0.1</sub>WO<sub>3</sub> (not shown).

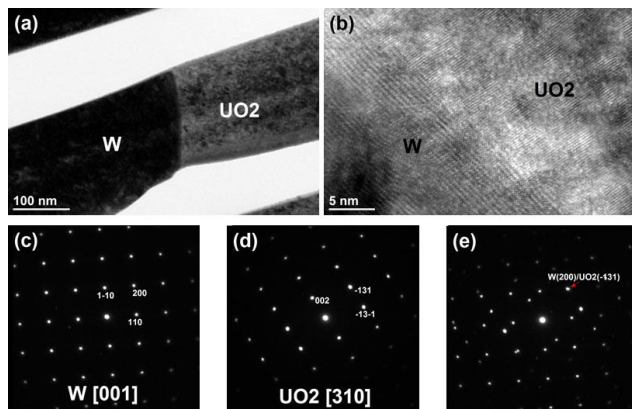


Fig. 1. TEM of W/UO<sub>2</sub> phase boundary

Fig. 2 shows an EDS line scan across the W/UO<sub>2</sub> boundary shown in figure 1. Fig. 2a shows the length of the line scan (50nm) and location of the line scan across the boundary. Fig. 2b is the corresponding concentration profiles calculated along the line scan. From fig. 2b it can be seen that the uranium (green line) extends approximately 15 nm into the tungsten. In all other sintered samples, the uranium migration was approximately 10 nm into the tungsten matrix.

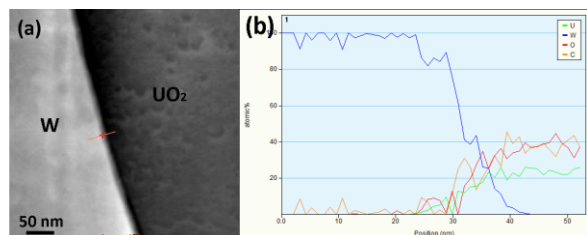


Fig. 2 EDS line scan of W/UO<sub>2</sub> boundary

Table II APT analysis of UO<sub>2</sub> particle

Ion	Atomic %	Atomic Error %
H	0.455937804	1.83E-03
C	4.001599093	1.36E-03
N	0.01180554	1.27E-03
O	62.9657518	1.02E-02
U	32.15545232	1.17E-03
Si	0.40945344	4.80E-03

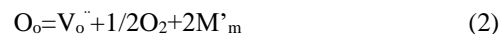
Atom probe tomography (APT) analysis was performed on all four samples. For the sample sintered at 1850°C, three dimensional elemental maps are shown in figure 3. It can be seen from fig. 3 that uranium and oxygen is present in the forms of UO, UO<sub>2</sub> and UO<sub>3</sub>. The nitrogen present is most likely from the nitrogen gas backfill used during the SPS

process. The only temperature where silicon was not observed was at 1750°C. Its origin is unknown but most likely is an impurity picked up during processing. There is also carbon present in the sample which is from the polyethylene binder used in the powder processing. The formula for the uranium oxide based on the APT data is given by UO<sub>1.95</sub> which is slightly substoichiometric. The samples sintered at 1600°C and 1700°C also had this formula while the sample sintered at 1750°C has the formula UO<sub>2</sub>.

The loss of uranium from the UO<sub>2</sub> particles and subsequent migration into the tungsten matrix can be understood in terms of generation of oxygen vacancies during sintering in a vacuum environment. Due to the loss of oxygen there are two possible defect reactions which can occur. The first is electronic compensation leading to the creation of oxygen vacancies and electrons. This reaction is given in equation 1.



Ionic compensation could lead to the formation of oxygen vacancies and reduction of the metal oxide on their sites as shown in equation 2.



The result of these reactions would be a substoichiometric uranium oxide and free uranium as given in equation 3.



This free uranium would then be available to diffuse into the tungsten matrix via Fick's Law of Diffusion either through the bulk or along grain boundaries.

It is very important to understand the effects of hot hydrogen on the cermet fuel. These cermets will be exposed to hydrogen gas in a thermal cycling environment. When thermal cycling takes place in a hydrogen environment, hydrogen permeates the tungsten matrix via grain boundary and bulk diffusion. The hydrogen can then combine with the free uranium and form uranium hydride. The free uranium has a melting point of ~1130°C and will rapidly diffuse along the tungsten grain boundaries and form UH<sub>3</sub> at ~225°C. The formation of UH<sub>3</sub> is accompanied by large increases in volume that can lead to tungsten grain separation creating avenues for subsequent migration of UO<sub>2</sub> to the cermet surface. [8] This migration results in loss of UO<sub>2</sub> and degradation of mechanical properties. We have performed preliminary studies on the SPS sintered W/UO<sub>2</sub> samples using our Compact Fuel Element Environmental Tester (CFEET). The CFEET has the capability of temperature close to 3000°K in a hydrogen environment. An initial run was made with the sample SPS sintered at 1800°C. The CFEET reached a temperature of 2273°K for

30 minutes. The mass was reduced by 0.05% by this test. It is planned to run these samples at higher temperatures in order to understand the effects of hot hydrogen on the chemical and structural properties of these W/UO<sub>2</sub> cermet.

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