PNNL-SA-117284



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# Theoretical Model for Volume Fraction of UC, <sup>235</sup>U Enrichment, and Effective Density of Final U-10Mo Alloy

April 2016

A Devaraj R Prabhakaran EJ McGarrah VV Joshi SY Hu CA Lavender



Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory Richland, Washington 99352

### **Purpose and Scope**

The purpose of this document is to provide a theoretical framework for (1) estimating uranium carbide (UC) volume fraction in a final alloy of uranium with 10 weight percent molybdenum (U-10Mo) as a function of final alloy carbon concentration, (2) estimating effective <sup>235</sup>U enrichment in the U-10Mo matrix after accounting for loss of <sup>235</sup>U in forming UC and (3) calculating effective density of as-cast U-10Mo alloy with varying enrichment. Therefore, this report will serve as the baseline for quality control of final alloy carbon content and <sup>235</sup>U enrichment.

# Acronyms and Abbreviations

C	carbon
FA	final alloy
HEU	highly enriched uranium
LEU	low-enriched uranium
Мо	molybdenum
PNNL	Pacific Northwest National Laboratory
SEM	scanning electron microscopy
U	uranium
U-10Mo	uranium alloyed with 10 weight percent molybdenum
UC	uranium carbide
UMo	body-centered cubic γ-UMo
<sup>235</sup> U Enrichment	Weight % of <sup>235</sup> U over total weight of U

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### 1.0 Introduction

The U.S. Department of Energy, National Nuclear Security Administration's Office of Material Management and Minimization requires the use of metallic fuel to meet the objectives of the Reactor Conversion Program (RC) for the fleet of United States High Performance Research Reactors. The metallic fuel selected to replace the current fuels is the low-enriched uranium (LEU), 10-weight percent molybdenum alloy in a thin sheet or foil form encapsulated in AA6061 aluminum alloy. The Fuel Fabrication Capability (FFC) pillar of RC has undertaken a series of tasks in order to meet performance and schedule requirements, and a series of projects have been undertaken that increase the understanding of the impact of processing conditions on the final fuel microstructure. Processing methods and chemistry of raw materials (highly enriched uranium (HEU) + U-Mo master alloy) can directly impact the final U-Mo LEU alloy quality, which is partially determined by the amounts of undesirable phases like carbides, MoSi<sub>2</sub>, or oxide phases in the final uranium with 10 weight percent molybdenum (U-10Mo) alloy product, and by the effective <sup>235</sup>U enrichment in the U-Mo matrix devoid of second phases. At present, a clear correlation between the final microstructure and the raw material chemistry or processing methods is lacking.

Hence, to support the FFC pillar's mission to establish quality benchmarks for fabricated U-10Mo LEU fuel, as a part of this report, mass balance calculations have been developed to estimate the carbide volume fraction in the final U-10Mo alloy as a function of carbon concentration. A related model has also been developed to estimate the final effective enrichment of <sup>235</sup>U in the U-Mo matrix of the U-10Mo alloy after accounting for loss of <sup>235</sup>U in carbide phase. These mathematical models were validated by comparing with detailed microstructural characterization and image processing results from Pacific Northwest National Laboratory (PNNL) and composition measurements provided by the Y-12 security complex. The carbide volume fraction and <sup>235</sup>U enrichment were then used to provide a direct estimation of the effective density of the final LEU fuel as a function of carbon concentration in the final U-10Mo alloy.

This report is expected to serve as the reference for carbide volume-fraction calculation, final effective <sup>235</sup>U enrichment calculation, and effective density calculation for the final U-10Mo alloy. The report is organized in the following sections.

Alloy Condition	Applicable Sections
Final U-10Mo Alloy	Section 2: Carbon Balance Model for Final Alloy Section 3: <sup>235</sup> U Enrichment Model for Final Alloy Section 4: Effective Density Calculation of Final Alloy Section 5: Future Work Section 6: References

### 2.0 Carbon Balance Model for Final Alloy

### 2.1 Motivation for Carbon Balance Modeling

Based on microstructure characterization results, the as-cast and homogenized U-10Mo final alloy (FA) received from Y-12 typically contains two phases: body centered cubic (BCC)-structured  $\gamma$ -UMo, hereafter called UMo phase, and uranium carbide (UC) phase (Burkes et al. 2009, 2010; Joshi et al. 2015a, 2015b). Based on backscattered electron scanning electron microscopy (SEM) images, the U-Mo phase appears to have grayscale contrast and UC appears to have dark black contrast (Figure 1). Using these contrast types, image processing can be done to isolate UC regions and estimate the area fraction (equivalent to volume fraction) of UC. The UC volume fraction in the FA has enormous implications on the quality of the FA due to its influence on subsequent mechanical processing, <sup>235</sup>U enrichment, and hence irradiation response. Recent works have shown that UC volume fraction in as-cast depleted-UMo ranges from 1–2% (Nyberg et al. 2013). At present, there is no model linking the carbon concentration in the FA with the volume fraction of this UC phase. Hence, a model needs to be developed that links the volume fraction of UC and the <sup>235</sup>U enrichment to the carbon concentration in the FA.



Figure 1. (a) SEM Secondary Electron Image of As-Cast and Homogenized U-10Mo Alloy Showing Dark Contrast from UC and Grayscale Contrast from UMo Phase; (b) the Same Area with UC Phase Regions Isolated using Image Contrast by Image Processing

Therefore, a model was developed to calculate the volume fraction of UC from the carbon concentration of 0-10,000 ppm in the FA.

Calculations to develop the carbon balance model consist of three steps:

- 1. estimating the number of U, Mo, and C atoms in UC phase and UMo phase in the FA as per the FA composition specifications
- 2. estimating the volume of UC and UMo phase per atom
- 3. estimating the volume fractions of UC and UMo phases.

# 2.2 Step 1: Estimating the Number of U, Mo, and C Atoms in UC Phase and UMo Phase in the FA as per the FA Composition Specifications

All calculations were done for 1,000 g of FA, and the FA composition is assumed to be  $U_{90-x}Mo_{10}C_x$  with 19.75 wt% of total U weight as <sup>235</sup>U. Based on this formula, the weight of each element in 1,000 g of FA was estimated for various carbon concentrations from 0 to 10,000 ppm.

Number of atoms of element =  $\frac{\text{weight of element} \times 6.023 \times 10^{23}}{\text{atomic mass}}$ 

Using this formula, the total number of atoms of <sup>235</sup>U, <sup>238</sup>U, Mo, and C in the FA was calculated for different values of carbon concentration in the FA.

Then, assuming zero solubility of C in the UMo matrix, all the C atoms in the FA are assumed to form UC.

Total number of atoms in UC phase = Total number of C atoms + same number of U atoms

Total number of atoms in UMo phase = Total U atoms - number of U atoms that formed UC + total number of Mo atoms

For the calculation of volume fraction of UC vs. C concentration, all the U in UC was assumed to be <sup>235</sup>U.

### 2.3 Step 2: Estimating Volume of UC and UMo Phase per Atom

Based on literature, UC is known to have a face-centered cubic structure with four formula units per unit cell (eight atoms per unit cell) and the lattice parameter taken from literature was 4.96 angstroms (Rundle et al. 1948, Austin 1959, Park et al. 2015). Based on this, the volume per atom for UC phase was calculated to be  $1.53 \times 10^{-29}$  m<sup>3</sup>.

U-10Mo phase is known to have BCC structure with two atoms per unit cell, with a lattice parameter of 3.41 angstroms (Burkes et al. 2009, Park et al. 2015). Based on this, the volume per atom for UMo matrix phase was calculated to be  $1.98 \times 10^{-29}$  m<sup>3</sup>.

### 2.4 Step 3: Estimating Volume Fractions of UC and UMo Phases

By multiplying the number of UMo and UC phase atoms calculated from Step 1 by the volume per atom for UC and UMo phases, respectively, from Step 2, the corresponding volumes and volume fractions can be obtained. A graph of carbon concentration vs. UC volume fraction shows a steady increase in UC phase volume fraction as a function of carbon concentration (Figure 2).



**Figure 2**. Volume Fraction of UC vs. Carbon Concentration in Final U-10Mo Alloy. The typical range of carbon concentration in FA of 300–1,200 ppm is marked by the red dashed-line oval, showing the volume fraction of UC to be between 0.5 and 3.5%.

Based on this model, the measured volume fraction of carbides is 0.5–3.5% for 300–1,200 weight ppm of carbon in the FA. This agrees very well with Y-12 reported carbon concentration and with PNNL image-processing–based carbide volume fraction measurements in the as-cast and homogenized FA (Nyberg et al. 2013).

<u>Supplementary information</u>: The worksheet with the entire calculation is provided in the attached Excel file named "Carbon balance\_Effective density\_29Feb2016.xlsx."

### 3.0 <sup>235</sup>U Enrichment Model for Final Alloy

LEU specifications call for a 19.75 % enrichment of <sup>235</sup>U in the FA. Enrichment is considered as 19.75 wt% of total weight of Uranium in final alloy. Hence in weight % it corresponds to 19.75% of 90%, which equals to 17.775 wt%. This <sup>235</sup>U is expected to come almost entirely from the HEU feedstock. The UC phase in the FA can either be preexisting from the HEU and stay undissolved during the mixing and melting processes, or it can be formed during the melting and casting stages. Depending upon when the UC phase forms, the ultimate <sup>235</sup>U enrichment in the UC phase and the UMo matrix can change. This final enrichment in the UMo matrix can also have a dependence on the volume fraction of UC phase in the FA, which in turn is dictated by the carbon concentration. Hence, we developed a model to predict the final effective enrichment of <sup>235</sup>U in UMo phase considering various enrichment cases of UC phase.

For simplicity, UC is assumed to have three different levels of enrichment:

- 0% enrichment, corresponding to pure <sup>238</sup>UC (case of DU-10Mo alloy)
- 100% enrichment, corresponding to pure <sup>235</sup>UC
- 19.75% enrichment, corresponding to UC with 19.75 wt% of total U in UC as <sup>235</sup>U.

The <sup>238</sup>UC consists of 50 at% <sup>238</sup>U and 50 at% C; in wt%, it is 95.1972 wt% <sup>238</sup>U and 4.8028 wt% C. Assuming 19.75 wt% of this total U is replaced with <sup>235</sup>U, the effective weight percent of low-enriched UC becomes 18.80144 wt% <sup>235</sup>U, 76.3957 wt% <sup>238</sup>U, and 4.8028 wt% C. In atom percent, this is 40.06 at% <sup>238</sup>U, 9.98 at% <sup>235</sup>U and 49.96 at% C. This means that, of the total number of U atoms in UC,

- 80.05% of the atoms will be  ${}^{238}$ U [ ${}^{238}$ U at%  $\div$  ( ${}^{238}$ U at% +  ${}^{235}$ U at%) × 100] and
- 19.95% will be <sup>235</sup>U atoms [<sup>235</sup>U at%  $\div$  (<sup>238</sup>U at% + <sup>235</sup>U at%)  $\times$  100].

To calculate the effective enrichment in the UMo matrix, first the number of U atoms that form UC is obtained from Step 1 in the carbon balance model. If 0% enrichment is assumed, all the <sup>235</sup>U is expected to go to UMo matrix; for 100% enrichment, all U atoms in UC are assumed to be <sup>235</sup>U and only the remaining <sup>235</sup>U (that is not in UC) goes to UMo matrix. For 19.75% enrichment, 80.05% of the U atoms in UC are assigned to <sup>238</sup>U, 19.95% are assigned to <sup>235</sup>U.

Based on the atom count balance for the three cases given above, the effective <sup>235</sup>U enrichment can be calculated as the ratio of the weight of <sup>235</sup>U in UMo matrix and total weight of U in UMo matrix of final alloy devoid of UC. The graph of <sup>235</sup>U enrichment in the UMo matrix as a function of carbon concentration (Figure 3) shows the upper bound for the <sup>238</sup>UC case (blue line), the lower bound for the <sup>235</sup>UC case (red line) and the 19.75 wt% <sup>235</sup>U in UC case (green line).



**Figure 3**. Enrichment of <sup>235</sup>U wt% in UMo Matrix of FA vs. Carbon Concentration Assuming Three Different Cases of Enrichment in UC. The typical carbon concentration range of 300–1,200 ppm is shown by the black dashed-line rectangle.

<u>Supplementary information</u>: The worksheet with the entire calculation is provided in the accompanying Excel file named "U235 enrichment calculations 29Feb2016.xlsx."

### 4.0 Effective Density Calculation of Final Alloy

In order to estimate density, the mass of a unit cell is divided by the volume of a unit cell.

### 4.1 Effective Density of UC

UC is face-centered cubic with eight atoms per unit cell (four U and four C atoms)

To estimate the mass of a unit cell of  $^{235}$ UC, the mass of four atoms of  $^{235}$ U is added to the mass of four atoms of C.

Mass of a <sup>235</sup>UC unit cell = 
$$\frac{4 \times 235.04}{6.023 \times 10^{23}} + \frac{4 \times 12}{6.023 \times 10^{23}}$$

From the lattice parameter of UC (4.96 angstroms), the volume of a unit cell is estimated and then used to estimate the densities of  $^{235}$ UC and  $^{238}$ UC.

Density of  ${}^{235}UC = \frac{Mass of a {}^{235}U unit cell}{Volume of unit cell} = 13.4394 grams/cm3$ 

Density of  $^{238}UC = 13.6031 \text{ grams/cm}3$ 

### 4.2 Effective Density of UMo Matrix

UMo is BCC with two atoms per unit cell and a lattice parameter of 3.41 angstroms.

To estimate the mass of UMo matrix, additional steps are necessary.

U-10Mo with no C is assumed to be 90 wt% U (17.775 wt%  $^{235}$ U + 72.225 wt%  $^{238}$ U) and 10 wt% Mo. Converted to atomic percent, these proportions become 15.649 at%  $^{235}$ U, 62.7825 at%  $^{238}$ U, and 21.5685 at% Mo.

The number of atoms per unit cell (two) was separated into the number of atoms of <sup>235</sup>U, <sup>238</sup>U, and Mo using the atomic percent values estimated above. Then the number of atoms of each element was multiplied by that element's individual atomic weight to obtain the total mass of a UMo unit cell. The resulting mass values and the lattice parameter were used to calculate the density of the UMo phase.

Density of UMo phase with 19.75 %  $^{235}U$  enrichment =  $\frac{Mass of \ a \ UMo \ unit \ cell}{Volume \ of \ unit \ cell}$ = 17.33187 grams/cm3

Density of UMo phase with no  $^{235}U = \frac{Mass of \ a \ UMo \ unit \ cell}{Volume \ of \ unit \ cell} = 17.36623 \ grams/cm3$ 

Now by using the calculated individual phase densities of the UMo matrix and the UC along with the volume fraction of UC phase, the effective density of the FA can be estimated by the rule of mixtures.

Effective density of final alloy = Density of UC × Volume fraction of UC + Density of UMo phase × (1 - volume fraction of UC)

In order to find the upper and lower bounds of effective density, four combinations are considered for the rule of mixtures:

- 1. Pure <sup>235</sup>UC with UMo matrix of 19.75 % <sup>235</sup>U enrichment: all UC in the alloy is <sup>235</sup>UC, and the matrix has a constant enrichment of 19.75 wt% <sup>235</sup>U out of total U.
- 2. Pure <sup>238</sup>UC with UMo matrix of 19.75 wt% <sup>235</sup>U enrichment: all UC in the alloy is <sup>238</sup>UC, and the matrix has constant enrichment of 19.75 wt% <sup>235</sup>U out of total U.
- 3. Pure <sup>235</sup>UC with no enrichment in the UMo matrix: all UC in the alloy is <sup>235</sup>UC, and the matrix is <sup>238</sup>U-10Mo only with no <sup>235</sup>U enrichment.
- 4. Pure <sup>238</sup>UC with no enrichment in the UMo matrix: all UC in the alloy is <sup>238</sup>UC and the matrix is <sup>238</sup>U-10Mo only with no <sup>235</sup>U enrichment.

These four cases will provide the outer envelope for effective density of the FA. In reality, for an FA with 19.75 % <sup>235</sup>U enrichment, the carbide phase can also have an enrichment of 19.75% or higher and hence the matrix

may have a slightly different effective <sup>235</sup>U enrichment. This case is expected to be in between the outer limits in a graph of these four cases (Figure 4).



Figure 4. Effective Density of Final Alloy Based on Rule of Mixtures

From the result of effective density in figure 4 it is clear that the green and purple lines are above the red and blue lines, thus the following relationships are clear:

- If the <sup>235</sup>U enrichment in the UMo matrix goes below 19.75%, the effective density increases.
- If the <sup>235</sup>U enrichment in the UC phase goes below 100% for a constant enrichment of matrix, the effective density increases.

Therefore, as long as the enrichment of the UMo matrix stays between 0 and 19.75 wt% <sup>235</sup>U, and the <sup>235</sup>U enrichment in UC phase stays between 0 and 100%, the effective density will fall within the band defined by the blue line and the green line in Figure 4. Only the presence of porosity or other impurity phases beyond UC will move the density beyond the limits shown in this graph.

<u>Supplementary Information</u>: The worksheet with the entire calculation is provided in the accompanying Excel file named "Carbon balance\_Effective density\_29Feb2016.xlsx."

### 5.0 Future Work

As a next step, we intend to experimentally measure the isotopic enrichment in the UC phase and the UMo matrix for as-cast FAs using atom probe tomography. We also intend to expand the carbon balance model to include silicon and oxygen balance to investigate the formation of MoSi<sub>2</sub> and UO<sub>2</sub> phases. Additionally, we will

be conducting detailed microstructural characterization of the FA to study the presence of other impurity elements and phases. An experimental density measurement system is also under development.

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