

Eutectoid Transformation in U10Mo Alloy: Effect of Deformation History and Homogenization Heat Treatment

January 2019

S Jana A Schemer-Kohrn N Overman L Sweet E Kautz C Lavender V Joshi



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

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights**. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY operated by BATTELLE for the UNITED STATES DEPARTMENT OF ENERGY under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062; ph: (865) 576-8401 fax: (865) 576-5728 email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service 5301 Shawnee Rd., Alexandria, VA 22312 ph: (800) 553-NTIS (6847) email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx> Online ordering: http://www.ntis.gov

Eutectoid Transformation in U10Mo Alloy: Effect of Deformation History and Homogenization Heat Treatment

January 2019

S Jana A Schemer-Kohrn N Overman L Sweet E Kautz C Lavender V Joshi

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

Pacific Northwest National Laboratory Richland, Washington 99352

Executive Summary

In the United States, uranium 10 wt.% molybdenum (U10Mo) alloy has been selected as the nuclear fuel that will be used when transitioning research reactors and radioisotope production facilities from highly enriched uranium (>85% ²³⁵U) fuel to low-enriched uranium (<20% ²³⁵U) fuel. The fabrication steps for producing U10Mo fuel foil involve multiple hot-rolling/cold-rolling/intermediate annealing steps. The U10Mo alloy, which can retain the desirable high-temperature body-centered cubic γ -U (A2) structure at room temperature as a metastable phase for optimum in-reactor performance, goes through a eutectoid reaction below ~560°C and forms α -U as a reaction product, which is highly undesirable. Because the fabrication steps are carried out in the temperature range of 500 to 700°C, it is critical to understand the eutectoid transformation behavior of various rolled/annealed U10Mo coupons at 450, 500, and 525°C. The results show that the highest degree of phase transformation occurs when the U10Mo billet is rolled down from the as-cast condition without any prior homogenization treatment. Further, we observed that mechanical deformation (in the form of hot-rolling/cold-rolling) leads to increased eutectoid transformation compared to the billets that were not deformed.

Acronyms and Abbreviations

body-centered cubic
discontinuous precipitation
electron back-scattered diffraction
inverse pole figure
National Institute of Standards and Technology Standard Reference Material
scanning electron microscopy
U-10 wt.% Mo
X-ray diffraction

Contents

Exec	cutive	e Summary	iii						
Acro	onym	s and Abbreviations	v						
1.0	Introduction								
2.0	Experimental Details								
3.0	Res	ults	5						
	3.1	XRD Analysis	5						
	3.2	EBSD Analysis							
	3.3	Summary of Eutectoid Transformation							
4.0	Con	clusions							
5.0	ReferencesError! Bookmark not defined.								

Figures

Figure 1. XRD Profiles of U10Mo Coupons in Rolled/Annealed Condition. The starting material was as-cast U10Mo billet	6
Figure 2. XRD Profiles of U10Mo Coupons in Rolled/Annealed Condition. The starting material was U10Mo billet homogenized at 900°C/48 h.	7
Figure 3. XRD Profiles of U10Mo Coupons in Rolled/Annealed Condition. The starting material was U10Mo billet homogenized at 1000°C/16 h.	8
Figure 4. IPF-X Map of U10Mo As-Cast Billet in Long-Transverse Cross Section as It is Rolled Down to 0.009 in. Thick Foil. Annealing was carried out at 700°C for 1 h	9
Figure 5. IPF-X Map of U10Mo As-Cast + 900°C/48 h Billet in Long-Transverse Cross Section as It is Rolled Down to 0.009 in. Thick Foil. Annealing was carried out at 700°C for 1 h.	9
Figure 6. IPF-X Map of U10Mo As-Cast + 1000°C/16 h Billet in Long-Transverse Cross Section as It is Rolled Down to 0.009" Thick Foil. Annealing was carried out at 700°C for 1 h.	10
Figure 7. Grain Size of γ-UMo Phase as a Function of Rolling/Annealing Operations	10
Figure 8. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 525°C/10 h of Isothermal Treatment. The starting material was as-cast U10Mo billet. (BSE-SEM image)	11
Figure 9. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 525°C/10 h of Isothermal Treatment. The starting material was as-cast +900°C/48 h homogenized U10Mo billet	12
Figure 10. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 525°C/10 h of Isothermal Treatment.\ The starting material was as-cast + 1000°C/16 h homogenized U10Mo billet	12
Figure 11. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 500°C/10 h of Isothermal Treatment. The starting material was as-cast U10Mo billet.	13
Figure 12. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 500°C/10 h of Isothermal Treatment. The starting material was as-cast 900°C/48 h homogenized U10Mo billet.	14
Figure 13. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 500°C/10 h of Isothermal Treatment. The starting material was as-cast 1000°C/16 h homogenized U10Mo billet	14
Figure 14. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 450°C/10 h of Isothermal Treatment. The starting material was as-cast U10Mo billet.	15
Figure 15. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 450°C/10 h of Isothermal Treatment. The starting material was as-cast 900°C/48 h homogenized U10Mo billet.	15
Figure 16. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 450°C/10 h of Isothermal Treatment. The starting material was as-cast 1000°C/16 h homogenized U10Mo billet	16
Figure 17. Effect of Homogenization Heat Treatment Time on DP-based Eutectoid Transformation. The least amount of transformation seen for 1000°C/60 h homogenization condition.	17
Figure 18. Degree of DP-Based Eutectoid Transformation at Three Temperatures in U10Mo Foil Coupon Obtained by Rolling the As-Cast Billet	17

1.0 Introduction

In the United States, uranium10 wt.% molybdenum (U10Mo) alloy has been selected as the nuclear fuel to be used when transitioning research reactors and radioisotope production facilities from highly enriched uranium (>85% ²³⁵U) fuel to low-enriched uranium (<20% ²³⁵U) fuel [1-4]. As a new class of metallic fuel, U10Mo alloy provides the required neutron flux and quality at less than 20% enrichment [4-9]. Compared to pure metallic uranium, which would provide the highest uranium density but has unfavorable burn-up characteristics in its room temperature orthorhombic crystal structure, α -U (e.g., high swelling during irradiation), U10Mo alloy is able to retain the high-temperature body-centered cubic (BCC) γ -U structure as a metastable phase at room temperature, and thus can offer the best combination of irradiation properties. Including Mo in the alloy allows the BCC crystal structure to be retained at room temperature.

According to the equilibrium phase diagram of the UMo system, the high-temperature γ -UMo phase (space group *Im3m*) decomposes into orthorhombic α -U (space group *Cmcm*) and body-centered tetragonal γ '-phase (U-₂Mo, space group *I4/mmm*) through a eutectoid transformation below the eutectoid temperature at ~560°C [10-13]. The eutectoid reaction in the UMo system initiates through a discontinuous precipitation (DP) or cellular reaction mechanism, which results in the formation of α -U + Mo-rich γ -UMo lamellar microstructure mostly along the prior γ -UMo grain boundaries [14-16]. It is generally accepted that the nature of this eutectoid reaction is quite sluggish, and as a result, the γ -UMo phase could be easily retained in its metastable condition even under very slow cooling conditions [17, 18]. However, for the fabrication of metallic monolithic UMo fuel foils, the as-cast UMo ingot is subjected to various rolling (hot-rolling/cold-rolling) and post-rolling steps such as hot isostatic pressing to form Al-UMo fuel clad. Most of these fabrication steps are carried between 500 and 700°C; therefore, during fabrication, the metastable γ -UMo phase that might prove deleterious during in-reactor operations [19, 20].

Because the eutectoid reaction in U10Mo alloy initiates through a DP mechanism, it is important to understand the factors that play a critical role in determining the DP reaction kinetics. The chemical composition of U10Mo alloy, especially the degree of chemical homogeneity of the matrix and presence/absence of impurity elements, would be a major factor because it is associated with the change in chemical free energy during transformation. According to information published in the literature, deformation is another important factor that governs DP kinetics, although the published results seem to vary based on the alloy system studied. The role of prior deformation in DP-based transformation in U10Mo alloy is unknown. However, from the fabrication perspective, it is very important to establish the role of various metal forming techniques on a DP-based eutectoid reaction in U10Mo alloy.

In this study, we report our findings on the effects of prior homogenization heat treatment schedules and the role of prior deformation through a combination of hot and cold-rolling and subsequent recrystallization annealing on DP-based eutectoid transformation kinetics in U10Mo. Previously, we reported the DP reaction kinetics of a commercially cast and homogenized U10Mo alloy at sub-eutectoid temperatures [21]. We also have reported the effects of the microstructure (prior γ -UMo grain size) on DP reaction kinetics [22] and the effects of systematically adding minor alloying constituents on DP in the U10Mo system [23-25]. This current report documents our latest efforts to understand the factors that govern the DP reaction in the U10Mo alloy system.

2.0 Experimental Details

In this study, we used as-cast U10Mo alloy billets to determine how DP reaction kinetics effect chemical composition/matrix homogeneity. We compared U10Mo alloy billets at three starting conditions: 1) as-cast, 2) homogenized at 900°C for 48 h, and 3) homogenized at 1000°C for 16 h. Homogenization heat treatment was carried out inside an argon (Ar)-atmosphere furnace to control uranium oxidation. The U10Mo billets (in either the as-cast condition or after homogenization at 900/1000°C) were subjected to a series of hot-rolling/intermediate-annealing/cold-rolling steps to fabricate fuel foils. Additionally 2 samples were homogenized at 1000 °C for 144 h and subsequently rolled down to 9 mils and annealed. These were the only processing steps where the phase transformation effect wasn't observed at each stage.

The various rolling/annealing steps are summarized below:



0.20 in. thick billet \rightarrow hot-rolled to 0.04 in. \rightarrow annealed at 700°C/l hr \rightarrow cold-rolled to 0.026 in. \rightarrow annealed at 700°C/l hr \rightarrow cold-rolled to 0.00k in." \rightarrow annealed at 700°C/l hr

Multiple samples were collected at each step of the rolling/annealing fabrication route for subsequent microstructural characterization/use as DP reaction coupons. The complete sampling scheme is shown in Table 1. The DP reaction kinetics were established by subjecting the rolled/annealed coupons to an isothermal treatment at 1) 525°C, 2) 500°C, and 3) 450°C for 10 h duration. For the isothermal treatment, U10Mo coupons were wrapped in zirconium-foil, and placed in an Ar-atmosphere furnace. The coupons were heated to the desired heat treatment temperature at a rate of 10°C/min and subsequently soaked at the desired heat treatment temperatures for 10 h. After the isothermal exposure, the furnace controller was turned off, and the U10Mo coupons cooled down to room temperature under controlled Ar-flow. The cooling rate between the sub-eutectoid heat treatment temperature and 200°C was estimated to be 2°C/min.

Scanning electron microscopy (SEM) imaging, electron back-scattered diffraction (EBSD), and X-ray diffraction (XRD) analysis were used to characterize samples. EBSD analysis was performed to estimate grain sizes using the linear intercept method on rolled/annealed U10Mo coupons. XRD analysis on rolled/annealed coupons was conducted to confirm the presence of γ -UMo phase at room temperature before subjecting the same coupons to multiple sub-eutectoid heat treatments. XRD data were collected using a Rigaku Ultima IV powder X-ray diffractometer equipped with a Cu x-ray tube operating at 40 kV and 40 mA, a vertical θ/θ goniometer with a 285 mm radius, and a D/teX linear position-sensitive silicon strip detector. A nickel filter was used to reduce the contribution of K β x-rays. An Eulerian cradle with automated sample height adjustment and sample rotation was used. Full pattern Rietveld refinement was performed using the TOPAS V5 software package (Bruker). Fundamental parameter type peak shapes were used in the refinement. The instrument contribution to peak broadening was determined by fitting three functions—1) a Lorentzian function with $1/\cos(\theta)$ dependence. 2) a hat function, and 3) a circle function with $1/\tan(\theta)$ dependence—to a diffraction pattern of National Institute of Standards and Technology Standard Reference Material (NIST SRM) 640d collected using the same slit settings as this sample. The instrument zero error was also determined using the NIST SRM 640d. A first-order Chebyshev polynomial with a 1/x function was used to model the background. Degrees of eutectoid transformation after sub-eutectoid heat treatment were determined from the SEM images [26]. Following sub-eutectoid temperature heat treatment, individual samples were mounted, ground, and polished to

 $0.05 \,\mu$ m finish using a standard metallographic procedure [27]. Microstructural examinations of the various U-Mo coupons were then carried out on a JEOL JSM-7600F SEM using the low-angle back-scattered electron detector for imaging. Image collection used a 30 keV electron beam with an approximate probe current of 6 nA and a working distance of 8 mm from the objective lens.

Condition	Hold for Metallography						450°C 10 h Heat Treatment						500°C 10 h Heat Treatment						525C for 10 h HT						
	As- Cast	Met ID	900°C hom	Met ID	1000°C hom	Met ID	As- Cast	Met ID	900°C hom	Met ID	1000°C hom	Met ID	As- Cast	Met ID	900°C hom	Met ID	1000°C hom	Met ID	As- Cast	Met ID	900°C hom	Met ID	1000°C hom	Met ID	
As-cast	Х	1199, 1200	х	1201, 1202	Х	1203, 1204	Х	1238	Х	1239	X	1240	х	1206, 1207	Х	1208, 1209	Х	1210, 1211	х	1181, 1182, 1205	х	1177, 1178	х	1179, 1180	
0.04 in. hot rolled	Х	DUM 1102, 1103	х	DUM 1104, 1105	X	DUM 1106, 1107	X	1259, 1260	X	1261, 1262			X	1183, 1184	х	1185, 1186			х	1151, 1152	Х	1153, 1154			
0.04 in. hot rolled + annealed at 700°C 1 hr	Х	1114, 1115	х	1116, 1117	Х	1118, 1119		1290, 1291		1292, 1293		1298, 1299	Х	1167, 1168		1294, 1295		1300, 1301	х	1155, 1156		1296, 1297		1302, 1303	
0.025 in. cold rolled	х	1108, 1109	х	1110, 1111	х	1112, 1113	х	1253, 1254	Х	1255, 1256	Х	1257, 1258	х	1193, 1194	х	1195, 1196	х	1197, 1198	х	1139, 1140	х	1143, 1144	х	1141, 1142	
0.025 in. cold- rolled + annealed @ 700°C 1 hr	X	1120, 1121	Х	1122, 1123	Х	1124, 1125																			
0.008 in. cold rolled	X	1127, 1128	х	1133, 1134	х	1135, 1136	х	1241, 1242	х	1243, 1244	X	1245, 1246	х	1187, 1188	х	1189, 1190	х	1191, 1192	х	1145, 1146	х	1149, 1150	х	1147, 1148	
0.008 in. cold- rolled + annealed	Х	1129, 1130	х	1131, 1132	х	1137, 1138	х	1247, 1248	х	1249, 1250	X	1251, 1252	Х	1169, 1170	х	1171, 1172	х	1173, 1174	х	1157, 1158, 1212, 1213	х	1159, 1160, 1214, 1215	х	1161, 1162, 1216, 1217	

Table 1. Complete Sampling Scheme

3.0 Results

3.1 XRD Analysis

XRD data from each of the rolled/annealed U10Mo coupons were collected at room temperature. Pure uranium goes through an allotropic transformation as it is cooled down from the high-temperature liquid phase to solid phase at room temperature (liquid U \rightarrow BCC U or γ -U, 1132°C \rightarrow complex tetragonal U or β-U, 772°C \rightarrow orthorhombic U or α-U, 662°C). However, through alloying with Mo, it is possible to retain the high-temperature BCC γ -U as a metastable phase at room temperature instead of α -U, even under very slow cooling conditions. In this study, we performed XRD analysis to confirm the presence of γ -UMo (BCC structure, A2) at room temperature in various rolled/annealed coupons. The effect of the initial microstructure/chemical homogeneity of the matrix on DP behavior, especially with successive plastic deformations through rolling, is the major focus of this study. In that regard, we examined three different initial conditions—1) as-cast U10Mo billet, 2) U10Mo billet homogenized at 900°C, and 3) U10Mo billet homogenized at 1000°C. XRD profiles of U10Mo coupons that were rolled to 0.009 in, thick foil using the three different starting materials are summarized in Figures 1 through 3. Detailed phase analysis using Reitveld refinement confirmed the presence of BCC γ -UMo as the major phase in all of the rolled/annealed U10Mo coupons. Additionally, the presence of a small amount of uranium carbide phase also was established. Some degree of preferred orientation was observed in the rolled samples (Figure 1d, 1f). Further, peak broadening and slight peak shifts were observed in coldrolled coupons because of significant lattice distortion due to deformation (Figure 1d, 1f). However, peaks become sharp after annealing due to recrystallization. XRD analysis of rolled coupons obtained from homogenized U10Mo billets showed very similar results. Therefore, the following conclusions can be drawn from the XRD analysis:

- BCC γ -UMo is the major phase present in rolled/annealed U10Mo coupons.
- Signs of preferred orientation is observed in cold-rolled U10Mo coupons irrespective of the starting microstructural condition (i.e., as-cast or homogenized).
- Intermediate annealing of cold-rolled coupons at 700°C for 1 h lead to (possibly complete [28, 29]) recrystallization and loss of preferred orientation.



Figure 1. XRD Profiles of U10Mo Coupons in Rolled/Annealed Condition. The starting material was as-cast U10Mo billet.



Figure 2. XRD Profiles of U10Mo Coupons in Rolled/Annealed Condition. The starting material was U10Mo billet homogenized at 900°C/48 h.



Figure 3. XRD Profiles of U10Mo Coupons in Rolled/Annealed Condition. The starting material was U10Mo billet homogenized at 1000°C/16 h.

3.2 EBSD Analysis

We used EBSD, which is a versatile, and highly reliable technique for determining grain size, for grain size analysis of rolled/annealed U10Mo coupons. The inverse pole figure (IPF) maps of the rolled/annealed U10Mo coupons in long-transverse cross section have been determined in this study. Evolution of grain structures for the 1) as-cast, 2) 900°C/48 h homogenized, and 3) 1000°C/16 h homogenized conditions are shown in Figures 4, 5, and 6, respectively. The grain size of the parent γ -UMo phase progressively decreases because of the repeated rolling operations. It appears that cold-rolling leads to the formation of elongated pancake shaped grains, which go through recrystallization during the

static intermediate annealing step and then become equiaxed. Additionally, we observed some signs of localized grain coarsening (abnormal grain growth) when the U10Mo as-cast billet was homogenized at 1000°C (Figure 6a).

Grain sizes of all of the U10Mo coupons after various processing conditions are summarized in Figure 7. It appears that the grain size of the 0.009 in. thick U10Mo foil after recrystallization annealing is $\sim 10 \,\mu$ m, irrespective of the starting condition of the billet (i.e., as-cast or homogenized). In addition, estimation of grain sizes in the 0.009 in. thick foil produced by cold-rolling could not be carried using the automated software because of severe strain in the microstructure. The presence of a high level of strain is apparent in IPF maps as indicated by the black areas (Figures 4f, 5f, 6f).



Figure 4. IPF-X Map of U10Mo As-Cast Billet in Long-Transverse Cross Section as It is Rolled Down to 0.009 in. Thick Foil. Annealing was carried out at 700°C for 1 h.



Figure 5. IPF-X Map of U10Mo As-Cast + 900°C/48 h Billet in Long-Transverse Cross Section as It is Rolled Down to 0.009 in. Thick Foil. Annealing was carried out at 700°C for 1 h.



Figure 6. IPF-X Map of U10Mo As-Cast + 1000°C/16 h Billet in Long-Transverse Cross Section as It is Rolled Down to 0.009" Thick Foil. Annealing was carried out at 700°C for 1 h.



Sample ID	Condition
1	As cast/ 900C-48 h/ 1000C-16 h
2	0.04" hot rolled
3	0.04" hot rolled and annealed @ 700C 1 h
4	0.025" cold rolled
5	0.025" cold rolled and annealed @ 700C 1 h
6	0.008" cold rolled
7	0.008" cold rolled and annealed @ 700C 1 h

Figure 7. Grain Size of γ -UMo Phase as a Function of Rolling/Annealing Operations

3.3 Summary of Eutectoid Transformation

Representative U10Mo coupons after various rolling/annealing operations were subjected to isothermal heat treatment at 525°C, 500°C, and 450°C for 10 h. The coupons then were imaged using SEM to determine the degree of eutectoid transformation. Because eutectoid transformation in U10Mo alloy initiates along the γ -UMo grain boundary through a DP-based mechanism, a lamellar microstructure is created. The lamellar microstructure consists of thin lamella of α -U, and Mo-enriched γ -UMo interlamellar regions. This kind of microstructure easily can be identified using back-scattered imaging in SEM [21-26]

1. Phase Transformation behavior at 525C-10hrs

Eutectoid transformation behavior after 525°C/10 h of heat treatment of rolled/annealed U10Mo coupons using the as-cast billet is shown in the series of SEM micrographs shown in Figure 8.



Figure 8. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 525°C/10 h of Isothermal Treatment. The starting material was as-cast U10Mo billet. (BSE-SEM image)

In the as-cast condition, the lack of compositional homogeneity in terms of Mo distribution is apparent in all of the micrographs in Figure 8, which is evident through the presence of relatively brighter (lower Mo concentration, higher U concentration) and darker (higher Mo concentration, lower U concentration) areas in the back-scattered SEM (BSE-SEM)images. In rolled samples, variations in the Mo concentration appear as banded areas. DP-based eutectoid transformation preferentially initiates in areas with low-Mo and high-U concentrations, as seen in the micrographs. Further, the degree of DP-based transformation increases as the thickness of the billet decreases during rolling. The progress of DP-based transformation after heat treatment at 525°C/10 h when the U10Mo billet is homogenized at 900°C for 48 h is shown in Figure 9.



Figure 9. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 525°C/10 h of Isothermal Treatment. The starting material was as-cast +900°C/48 h homogenized U10Mo billet.

Compared to the as-cast billet, the degree of eutectoid transformation is markedly less after the 900°C homogenization treatment. In addition, signs of Mo concentration variations are absent after the homogenization treatment. However, some signs of banding is apparent in 0.008 in. cold-rolled foil after annealing. Further, it is interesting to note that the degree of DP-based transformation is higher in the 0.008 in. cold-rolled foil after annealing, compared to just cold-rolling. The nature of eutectoid transformation after 525°C/10 h heat treatment as a function of rolling/annealing steps after homogenization at 1000°C for 16 h is shown in Figure 10.



Figure 10. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 525°C/10 h of Isothermal Treatment. The starting material was as-cast + 1000°C/16 h homogenized U10Mo billet.

Similar to previous observations, the degree of eutectoid transformation is limited after homogenization at 1000°C is applied to the as-cast U10Mo billet. Once again, there is a difference in the degree of transformation in the 0.008 in. foil, with the foil that was only cold-rolled showing relatively less transformation in comparison to cold-rolled + annealed condition.

2. Phase Transformation behavior at 500C-10hrs

The progression of eutectoid transformation after 500°C/10 h of heat treatment of rolled/annealed U10Mo coupons using the 1) as-cast billet, 2) 900°C/48 h homogenized billet, and 3) 1000°C/16 h homogenized billet is shown in Figures 11 through 13, respectively. The degree of eutectoid transformation is noted to be less after heat treatment at 500°C compared to heat treatment at 525°C. We are currently developing an automated image analysis technique to evaluate the degree of phase transformation as a function of processing conditions. Among the three starting billet conditions (i.e.., as-cast, 900°C/48 h homogenized, and 1000°C/16 h homogenized), the highest amount of eutectoid transformation was observed in the as-cast billet. Additionally, we found the degree of transformation to be higher in 0.008 in./0.009 in. thick foil produced from the billet after cold-rolling + annealing compared to the material that had been cold-rolled only.



Figure 11. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 500°C/10 h of Isothermal Treatment. The starting material was as-cast U10Mo billet.



Figure 12. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 500°C/10 h of Isothermal Treatment. The starting material was as-cast 900°C/48 h homogenized U10Mo billet.



Figure 13. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 500°C/10 h of Isothermal Treatment. The starting material was as-cast 1000°C/16 h homogenized U10Mo billet.

3. Phase transformation behavior at 450C/10 hrs

Eutectoid transformation behavior of three starting billet conditions after 450°C/10 h heat treatment is shown in Figures 14 through 16. The degree of transformation was observed to be the least after heat

treatment at 450°C. The rest of our findings are very similar to what was observed after 500°C/525°C heat treatment in terms of the relationship between the degree of DP transformation and processing steps.



Figure 14. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 450°C/10 h of Isothermal Treatment. The starting material was as-cast U10Mo billet.



Figure 15. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 450°C/10 h of Isothermal Treatment. The starting material was as-cast 900°C/48 h homogenized U10Mo billet.



Figure 16. Eutectoid Transformation Behavior in U10Mo Coupons as a Function of Rolling/Annealing Steps after 450°C/10 h of Isothermal Treatment. The starting material was as-cast 1000°C/16 h homogenized U10Mo billet.

In summary, it appears that the degree of eutectoid transformation in U10Mo alloy is primarily determined by the chemical homogeneity of the matrix. At any one of the three sub-eutectoid temperature heat treatment conditions, highest degree of transformation was observed in U10Mo coupons obtained by rolling the as-cast billet. Homogenization of the billet at 900/1000°C helps in lowering the amount of phase transformation because the Mo concentration distribution is more uniform. Further, rolling promoted DP-based phase transformation, which might be related with the generation bands, etc., most likely provide new nucleation sites, leading to increased DP reaction. However, we also noted that when a foil remains in a cold-rolled condition, less DP-based transformation occurs when compared to foil that was cold-rolled + annealed. This aspect of DP should be studied in more detail to understand the underlying mechanisms.

Because homogenization helped reduce the degree of eutectoid transformation, two more homogenization treatments were carried out—one at 900°C/144 h and another at 1000°C/60 h. The homogenized billets then were rolled to 0.008 in./0.009 in. thick foil as previously described. To elucidate the effect of longer duration homogenization treatments on DP behavior, we compared micrographs obtained from heat treated 0.008 in. thick cold-rolled + annealed U10Mo coupons (see Figure 17).



Figure 17. Effect of Homogenization Heat Treatment Time on DP-based Eutectoid Transformation. The least amount of transformation seen for 1000°C/60 h homogenization condition.

For comparison, Figure 18 shows the condition of the foil coupons obtained by rolling the as-cast. It can be clearly seen that with longer duration heat treatment at both the temperatures (900°C and 1000°C), the degree of DP-based eutectoid transformation decreases. Because the recrystallized grain size at all four studied conditions—1) 900°C/48 h, 2) 900°C/144 h, 3) 1000°C/16 h, and 4) 1000°C/60 h—are similar, (i.e., ~11µm), this variation in the degree of DP transformation is associated with the chemical homogeneity of the parent γ -UMo phase only. In this regard, an in-depth comparative diffusivity study of these microstructures would be very valuable for optimizing the UMo foil fabrication process.



Figure 18. Degree of DP-Based Eutectoid Transformation at Three Temperatures in U10Mo Foil Coupon Obtained by Rolling the As-Cast Billet. Significantly higher transformation was noted when compared to homogenized conditions.

4.0 Conclusions

In this study, we identified DP-based eutectoid transformation behavior in rolled/annealed U10Mo coupons at three sub-eutectoid temperatures—450, 500, and 525°C. We examined three different conditions of the starting U10Mo billet—1) as-cast, 2) homogenized at 900°C/48 h, and 4) homogenized at 1000°C/16 h. Our major findings are briefly described below:

- We observed the highest degree of transformation when the rolled/annealed U10Mo coupons obtained from the as-cast billet had been subjected to sub-eutectoid heat treatment.
- Homogenization heat treatment helps reduce the degree of DP-based transformation.
- Higher homogenization treatment temperatures results in less DP-based transformation.
- Increasing the time duration of homogenization treatment helps further reduce the degree of DP-based transformation.
- More DP-based reactions occur in materials that had been deformed than in materials that had not been deformed.
- A higher degree of DP-based reaction is noticed in material that had been cold-rolled + annealed than in material that had been cold-rolled only.

5.0 References

[1] J.L. Snelgrove, G.L. Hofman, M.K. Meyer, C.L. Trybus, T.C. Wiencek, Development of very-highdensity low-enriched-uranium fuels1Work supported by the US Department of Energy, Office of Nonproliferation and National Security, under contract No. W-31-109-ENG-38.1, Nuclear Engineering and Design 178(1) (1997) 119-126.

[2] D.E. Burkes, R. Prabhakaran, T. Hartmann, J.-F. Jue, F.J. Rice, Properties of DU–10wt% Mo alloys subjected to various post-rolling heat treatments, Nuclear Engineering and Design 240(6) (2010) 1332-1339.

[3] Frost. B, Nuclear Materials. Materials Science and Technology - A Comprehensive Treatment, First ed., VCH, Weinheim, 1994.

[4] M.K. Meyer, J. Gan, J.F. Jue, D.D. Keiser, E. Perez, A. Robinson, D.M. Wachs, N. Woolstenhulme, G.L. Hofman, Y.S. Kim, IRRADIATION PERFORMANCE OF U-Mo MONOLITHIC FUEL, Nuclear Engineering and Technology 46(2) (2014) 169-182.

[5] K. Kim, D.B. Lee, C.K. Kim, I.H. Kuk, K.W. Baek, Development of uranium-silicide and U-Mo alloy fuels by centrifugal atomization, International Atomic Energy Agency (IAEA), 1997, pp. 77-86.

[6] K.H. Kim, D.B. Lee, C.K. Kim, G.E. Hofman, K.W. Paik, Characterization of U-2 wt% Mo and U-10 wt% Mo alloy powders prepared by centrifugal atomization, Journal of Nuclear Materials 245(2) (1997) 179-184.

[7] P.V.H. V.P. Sinha, G.J. Prasad, H.S. Kamath, Seventeenth Plansee Seminar, Reutte, Austria, 2009, pp. RM 78/1-16.

[8] S. Hu, D. Burkes, C.A. Lavender, V. Joshi, Effect of grain morphology on gas bubble swelling in UMo fuels – A 3D microstructure dependent Booth model, Journal of Nuclear Materials 480 (2016) 323-331.

[9] S. Hu, W. Setyawan, V.V. Joshi, C.A. Lavender, Atomistic simulations of thermodynamic properties of Xe gas bubbles in U10Mo fuels, Journal of Nuclear Materials 490 (2017) 49-58.

[10] A.E. Dwight, The uranium-molybdenum equilibrium diagram below 900° C, Journal of Nuclear Materials 2(1) (1960) 81-87.

[11] Binary Alloy Phase Diagrams-Second edition, ASM International, Materials Park, Ohio, USA, 1990.
[12] X. Zhang, Y.F. Cui, G.L. Xu, W.J. Zhu, H.S. Liu, B.Y. Yin, Z.P. Jin, Thermodynamic assessment of the U–Mo–Al system, Journal of Nuclear Materials 402(1) (2010) 15-24.

[13] A. Berche, N. Dupin, C. Guéneau, C. Rado, B. Sundman, J.C. Dumas, Calphad thermodynamic description of some binary systems involving U, Journal of Nuclear Materials 411(1) (2011) 131-143.
[14] S. Neogy, M.T. Saify, S.K. Jha, D. Srivastava, M.M. Hussain, G.K. Dey, R.P. Singh, Microstructural

study of gamma phase stability in U–9wt.% Mo alloy, Journal of Nuclear Materials 422(1) (2012) 77-85.

[15] M.T. Saify, S.K. Jha, D. Srivastava, G.K. Dey, Ageing characteristics of the metastable gamma phase in U–9 wt.% Mo alloy: experimental observations and thermodynamic validation AU - Neogy, S, Philosophical Magazine 95(26) (2015) 2866-2884.

[16] S. Saubert, R. Jungwirth, T. Zweifel, M. Hofmann, M. Hoelzel, W. Petry, Neutron and hard X-ray diffraction studies of the isothermal transformation kinetics in the research reactor fuel candidate U-8 wt% Mo, Journal of Applied Crystallography 49(3) (2016) 923-933.

[17] R.G. Repas PE, and RF Hehemann, TRANSFORMATION CHARACTERISTICS OF U-Mo AND U-Mo-Ti ALLOYS, Trans. Am. Soc. Metals 57 (1964).

[18] M.A. Steiner, C.A. Calhoun, R.W. Klein, K. An, E. Garlea, S.R. Agnew, α -Phase transformation kinetics of U – 8 wt% Mo established by in situ neutron diffraction, Journal of Nuclear Materials 477 (2016) 149-156.

[19] A. Soulami, D.E. Burkes, V.V. Joshi, C.A. Lavender, D. Paxton, Finite-element model to predict roll-separation force and defects during rolling of U-10Mo alloys, Journal of Nuclear Materials 494 (2017) 182-191.

[20] G. Cheng, X. Hu, W.E. Frazier, C.A. Lavender, V.V. Joshi, Effect of second phase particles and stringers on microstructures after rolling and recrystallization, Materials Science and Engineering: A 736 (2018) 41-52.

[21] S. Jana, A. Devaraj, L. Kovarik, B. Arey, L. Sweet, T. Varga, C. Lavender, V. Joshi, Kinetics of cellular transformation and competing precipitation mechanisms during sub-eutectoid annealing of U10Mo alloys, Journal of Alloys and Compounds 723 (2017) 757-771.

[22] S. Jana, N. Overman, T. Varga, C. Lavender, V.V. Joshi, Phase transformation kinetics in rolled U-10 wt. % Mo foil: Effect of post-rolling heat treatment and prior γ -UMo grain size, Journal of Nuclear Materials 496 (2017) 215-226.

[23] A. Devaraj, E. Kautz, L. Kovarik, S. Jana, N. Overman, C. Lavender, V.V. Joshi, Phase transformation of metastable discontinuous precipitation products to equilibrium phases in U10Mo alloys, Scripta Materialia 156 (2018) 70-74.

[24] A. Devaraj, L. Kovarik, E. Kautz, B. Arey, S. Jana, C. Lavender, V. Joshi, Grain boundary engineering to control the discontinuous precipitation in multicomponent U10Mo alloy, Acta Materialia 151 (2018) 181-190.

[25] S. Jana, L. Sweet, D. Neal, A. Schemer-Kohrn, C. Lavender, V. Joshi, The role of ternary alloying elements in eutectoid transformation of U10Mo alloy part I. Microstructure evolution during arc melting and subsequent homogenization annealing in U9.8Mo0.2X alloy (X = Cr, Ni, Co), Journal of Nuclear Materials 509 (2018) 318-329.

[26] S.J. A Devaraj, CA McInnis, NJ Lombardo, VV Joshi, LE Sweet, Detecting the Extent of Eutectoid Transformation in U-10Mo, Pacific Northwest National Laboratory (PNNL), Richland, WA (US).
[27] V.J. R Prabhakaran, MA Rhodes, AL Schemer-Kohrn, AD Guzman, U-10Mo Sample Preparation and Examination using Optical and Scanning Electron Microscopy, Pacific Northwest National Lab.(PNNL), Richland, WA (United States).

[28] W.E. Frazier, S. Hu, N. Overman, C. Lavender, V.V. Joshi, Short communication on Kinetics of grain growth and particle pinning in U-10 wt.% Mo, Journal of Nuclear Materials 498 (2018) 254-258.
[29] W.E. Frazier, S. Hu, N. Overman, R. Prabhakaran, C. Lavender, V.V. Joshi, Recrystallization kinetics of cold-rolled U-10 wt% Mo, Journal of Nuclear Materials 513 (2019) 56-61.



www.pnnl.gov

902 Battelle Boulevard P.O. Box 999 Richland, WA 99352 1-888-375-PNNL (7665)

