The Effect of Low-Temperature Aging on the Microstructure and Deformation of Uranium- 6wt% Niobium: An In-Situ Neutron Diffraction Study

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ABSTRACT

The mechanical properties of uranium-niobium alloys evolve with aging at relatively low temperatures due to subtle microstructural changes. *In-situ* neutron diffraction measurements during aging of a monoclinic U-6Nb alloy at temperatures to 573 K were performed to monitor these changes. Further, *in-situ* neutron diffraction studies during deformation of U-6Nb in the as-quenched state and after aging for two and eight hours at 473 K were completed to assess the influence of microstructural evolution on mechanical properties. With heating, large anisotropic changes in lattice parameter were observed followed by relaxation with time at the aging temperature. The lattice parameters return to nearly their initial values with cooling. The active plastic deformation mechanisms including, in order of occurrence, shape-memory de-twinning, mechanical twinning, and slip-mediated deformation do not change with prior aging. However, the resistance to motion of the as-quenched martensitic twin boundaries increases following aging, resulting in the observed increase in initial yield strength.

I. Introduction

The crystal structure of solid pure uranium at high temperature ($1049\text{ K} < T < 1405\text{ K}$) is body-centered cubic (γ phase) [1]. On cooling, uranium experiences a solid-solid phase transformation to the tetragonal β phase followed by a second transformation to an orthorhombic α phase, which is stable at room temperature. To improve the room temperature mechanical properties and corrosion resistance, attempts have been made to alloy uranium with other elemental metals such as Mo [2, 3], Nb [4], Zr [5] and Ti [6, 7], each of which is soluble in the high temperature γ phase. Although these elements have minimal solubility in the β or α phases of uranium, metastable martensitic phases can be formed by moderate to rapid quenching from the high-temperature γ phase. The addition of niobium to uranium is of particular interest because it significantly increases the oxidation resistance and increases the ductility [8].

When quenched from high temperatures to prevent diffusional decomposition, the uranium-niobium alloy system has a rich metastable phase diagram [4, 9-13]. At low niobium ($[\text{Nb}] < 3.5\text{ wt\%}$) content the metastable alloy has an α' orthorhombic structure, similar to pure uranium, with an expanded **b** and contracted **a** lattice parameter. As niobium content is increased to intermediate values ($3.5\text{ wt\%} < [\text{Nb}] < 6.5\text{ wt\%}$), the alloy assumes an α'' monoclinic structure that is characterized by an increase of the γ angle of the orthorhombic structure. Further niobium enrichment ($6.5\text{ wt\%} < [\text{Nb}] < 9\text{ wt\%}$) yields a tetragonal distortion of the body-centered cubic structure of γ -U, termed γ° . Finally, above roughly 9 wt% niobium the bcc γ phase is retained to room temperature with quenching. The transformation temperatures between the phases during quenching and heating of alloys with up to 10 wt% niobium have recently been reported [14], but

early studies indicated that both the austenitic and martensitic transformations were dependent on heating and/or cooling rate [9]. The lattice parameters of each phase have been determined with x-ray diffraction and reported [4, 10, 11].

The deformation of U-Nb alloys in the α'' phase field (near 6 wt%) have been studied extensively [15-18] because the superior corrosion resistance and ductility of this particular composition leads to use in several applications. In-situ neutron diffraction during deformation to monitor the evolution of crystallographic texture with tensile deformation [18] coupled with ex-situ electron microscopy studies [19, 20] have shown that U-6wt%Nb (U-6Nb) exhibits distinct dominant deformation mechanisms, detwinning of martensitic variants formed during transformation, formation of mechanical twins, and finally slip mediated deformation, with increasing strain.

It is well known that U-Nb alloys near 6wt% are age hardenable by heat treatments well below the 920 K monotectoid. Aging at temperature greater than roughly 575 K results in significant hardening with corresponding loss of ductility and loss of corrosion resistance [8]. The hardening is due to non-lamellar precipitation at early time followed by cellular decomposition of the α'' toward the equilibrium phases of niobium-poor α and niobium-rich γ phase [8, 9, 21-25] at long times. However, significant hardening is also observed after aging at temperatures as low as 475 K [23, 26], but experimental determination of the mechanism of this low temperature hardening has remained elusive [23, 26]. Using transmission electron microscopy (TEM), Hsiung interprets the microstructural evolution (at nominally 6 wt%Nb) as being consistent with spinodal decomposition after aging at 473 K for as little as 16 hours. In contrast, Clarke et al. [23] did not observe statistically relevant chemical heterogeneity (beyond their

quoted uncertainty of 1%) with atom probe tomography at the nm scale after as much as 70 days at 473 K, which is inconsistent with spinodal decomposition. It is worth noting that Clarke et al. did observe significant chemical variations after aging at a higher temperature, 573 K, which is consistent with prior work at this temperature [8, 9, 21, 22, 27, 28]. Moreover, a thermodynamics-based argument against spinodal decomposition as a low temperature aging mechanism was presented by Clarke et al. [23].

In order to better understand the microscopic origins of the aging process and the concomitant change in mechanical response, we have carried out *in-situ* neutron diffraction measurements: (1) during low temperature aging of a U-6Nb alloy at 373 K, 473 K, 523 K, and 573 K for up to 40 hours, and (2) during deformation of U-6Nb in the as-quenched condition as well as after aging at 473 K. As probe particles, neutrons have an advantage over x-rays and electrons in that they penetrate distances on the order of centimeters into most materials, including uranium. This allows the bulk microstructure (as opposed to a surface layer) to be monitored while under non-ambient conditions. Changes in lattice parameters during heating which are large compared to the expected thermal expansion of α -U are observed, followed by time dependent relaxation of the lattice parameter during subsequent isothermal holds. Moreover, based on the evolution of the texture, we find that, while the initial yield strength of the material increases after low temperature aging (473 K), the active deformation mechanisms do not change. The motion of transformation twin boundaries, which is responsible for the initial yield phenomenon [17, 18] becomes more difficult, but remains the predominant active deformation mode at small strains. However, the current data cannot unambiguously

identify the microscopic mechanism of the increased resistance to motion of the transformation twin boundaries with low temperature aging.

II. Experimental Details

A. Sample Preparation

Two different sources of nominally U-6Nb material were used for the experiments [14]. Niobium concentration-dependence and aging experiments were performed on samples made in small batches specifically intended to yield (compositionally) homogenized samples [14, 29]. Small-scale (~50 gram) U-Nb alloy buttons were synthesized by arc melting high-purity, unalloyed depleted uranium and elemental niobium under an argon partial pressure. The challenges of mixing elements with dissimilar melting points and densities required progressive additions of the U charge to the Nb, which required about 30 melting steps. After the final melt, a portion of the button was cut off, re-melted, and suction cast into a 5-mm-diameter rod, resulting in rapid quenching to minimize micro-segregation. The rod was then homogenized for 100 hours at 1273 K under vacuum and water quenched. A total of 41 alloys were made, with nominal compositions separated by 0.25 wt% increments that spanned 0–10 wt% Nb. Chemical analyses of the final rods, as determined by direct current plasma emission spectroscopy, are shown in Table 1. Throughout this work, these samples will be referred to as homogenized U-6Nb [14].

For the deformation experiments, samples were machined from plates that were produced in large quantities. Cast uranium and strip niobium were vacuum induction melted and cast in an yttria-coated graphite crucible. The ingot then underwent a double vacuum arc re-melting procedure, in which the ingot was the consumable electrode. The

double arc-cast ingot was homogenized for 18 hours at 1373 K in vacuum. Pucks, 64 mm thick and 190 mm in diameter, were cut and machined from the homogenized ingot. The pucks were cold rolled under argon at 1123 K to a final thickness of 9 mm using ~13% reduction per pass. The pucks were then solutionized at 1123 K for 4 hours under vacuum, and oil quenched. Because of the larger scale of the production process, chemical inhomogeneity within the specimens persisted in the form of Nb bands of amplitude 4-8 wt% Nb, with length scale on the order of 100 microns. Wet chemical analysis of a sample indicated that the final niobium content was actually 5.77 wt%. This pedigree of material has been referred to in the literature as banded U-6Nb [14]. Complete chemical analysis of the banded material can also be found in Table 1.

Pin-holed flat dog-bone tensile samples were machined with a gauge cross section of 6.35 x 2.5 mm and gauge length of 50 mm (ASTM Standard A370-09). Two tensile specimens underwent aging heat treatments at 473 K for 2 and 8 hours and water quenched, while one was maintained in the solutionized and quenched condition.

B. Neutron Diffraction

The dependence of the structure and lattice parameters of the U-Nb alloy system on the niobium concentration was measured on the Neutron Powder Diffractometer (NPD), while the *in-situ* accelerated aging and deformation measurements were completed on the Spectrometer for MAterials Research at Temperature and Stress (SMARTS). Both diffractometers are at the Lujan Neutron Scattering Center at LANL. NPD [30] and SMARTS [31] are similar and may be described concurrently. Both diffractometers accept a pulsed white beam (useful range from 0.5 to 4 Å) of neutrons generated through spallation reactions in a tungsten target and moderated by a water

moderator at 283 K. SMARTS has a neutron guide along much of the incident flight path, increasing the incident beam flux on the sample by roughly five times, at a small cost in resolution and beam divergence. In both cases, the incident neutron beam is comparable to the size of the sample (or gauge section of the tensile sample), essentially bathing the sample in the neutron beam.

The homogenized U-6Nb samples were placed in the center of either diffractometer, roughly 30 m from the moderator. Both instruments have detector banks consisting of ^3He filled tubes located 1.5 to 2 m from the sample in the horizontal plane at $\pm 90^\circ$ relative to the incident beam. Spectra from individual tubes are summed, with corrections applied for differences in diffraction angle and flight path (time-focused), to provide a single integrated diffraction pattern for each detector bank. Due to the pulsed time structure and continuous energy spectrum of the incident beam, the time-of-flight (TOF) technique can be used to record an entire diffraction pattern in a single detector bank; that is with a co-linear diffraction vectors.

On NPD, diffraction patterns were recorded from 40 samples with niobium concentration between 0.25 and 10 weight percent (wt%) [29]. The samples were manually placed in the diffractometer with their cylinder axis vertical, which introduces some sample positioning uncertainty that is greater than the statistical uncertainty inherent in the fitting of diffraction patterns.

In-situ aging experiments at 373 K, 473 K, 523 K and 573 K were performed on homogenized U-6Nb material in SMARTS [31] in a vacuum ($\sim 10^{-6}$ Torr) furnace heated by tungsten wire meshes above and below the sample position. The furnace temperature was controlled by a thermocouple in close proximity to the sample. A second

thermocouple in mechanical contact with the sample recorded the sample temperature. The solutionized and quenched samples were heated to the desired aging temperature as quickly as possible without overshooting. Because the radiative coupling between the sample and the furnace is relatively weak (especially at the lowest temperatures studied), the heating time was typically ~30 minutes at a roughly constant rate. Upon reaching the aging temperature, the sample temperature was held constant to within $\pm 2\text{K}$ for the duration of the experiment. A single diffraction pattern of sufficient quality to complete Rietveld refinement of the lattice parameters was achieved with 3 minutes of counting. Patterns were collected continuously for up to 36 hours at temperature. Typically, the count time was increased to 20 minutes after the kinetics of the microstructural evolution retarded (~3 hours).

Data was also collected with ~3 minute resolution during cooling in the vacuum furnace. A neutron beam loss during the 373 K aging ended that particular test at roughly 20 hours and no data was collected on cooling. Likewise, the 473 K aging experiment was interrupted by a beam loss, but this sample was maintained at temperature during the outage and diffraction data was collected during cooling to room temperature.

Room temperature in-situ deformation experiments were completed on banded U-6Nb alloy samples on the SMARTS diffractometer on solutionized and quenched material, material aged (ex-situ) at 473 K for two hours and eight hours. The samples were deformed in a horizontal custom built load frame, with the load axis oriented at 45° relative to the incident beam, such that the detectors on either side of the specimen recorded data with diffraction vectors parallel ($\mathbf{Q}_{\parallel}$) and transverse ($\mathbf{Q}_{\perp}$), to the applied load simultaneously [31]. An extensometer was used to determine macroscopic

engineering strain and load measured by a load cell during the deformation tests. A cadmium mask was used to shield the steel knife edges of the extensometer from the incident neutron beam. However, in the case of the sample aged for eight hours at 473 K, the mask was placed too low and the steel (110) peak appears in the diffraction pattern at $2.03\text{\AA}$. In what follows, the results are plotted as a function of true stress, $\sigma_T = \sigma_E(1 + \varepsilon_E)$ and true strain, $\varepsilon_T = \ln(\varepsilon_E + 1)$.

C. Data Analysis

Rietveld analysis and single peak fitting were completed on the diffraction data using the General Structural Analysis System (GSAS) software package developed at Los Alamos [32]. For the α' and α'' structures, the space group utilized in the analysis was (C 1 1 2₁/m) with 2 equivalent atom positions, (x, y, z) and (-x, -y, z + 1/2), each with a multiplicity of 4. The non-conventional space group facilitated comparison of the low niobium concentration orthorhombic phase with the monoclinic phase at intermediate niobium concentrations, with the transformation being manifested by the deviation of the angle between the **a** and **b** lattice vectors from 90°. The peak positions of the body centered tetragonal γ_0 phase were calculated from the P 4/n m m space group with a = 4.946Å and c = 3.373Å found for U-7Nb in previous work [33].

To accommodate anisotropic peak broadening, a peak profile function that allowed for variation of the peak width depending on the crystallographic direction was utilized in the Rietveld refinement [34]. The crystallographic texture was modeled by GSAS using an 8th order spherical harmonics expansion of the orientation distribution function. The coefficients of the spherical harmonics are determined by fitting the calculated peak intensities to those observed. In addition to Rietveld refinement, single-

peak fitting was completed using the Von Dreele, Jorgensen, and Windsor convolution profile function [35] embedded in GSAS.

Rietveld refinement has the advantage that more accurate lattice parameters and texture information are obtained with data of lesser statistical quality because the entire pattern is fit to a constrained structural model. However, the lattice parameters so determined are the result of an “empirical average” over all of the grains and crystal orientations that contribute to the diffraction pattern. In contrast, single peak fits provide the interplanar spacing of a specific set of atomic planes in a family of grains with common orientation with respect to the diffraction vector, and are thus more easily interpreted.

C.1. Inverse Pole Figures

Whereas pole figures map the density of a single crystallographic plane normal (pole) with respect to sample direction, inverse pole figures (IPF) map the density of all poles (hkl) along a particular sample orientation (e.g. the rolling, transverse, and normal directions of a rolled plate). This particular projection of the orientation distribution function is well suited to TOF diffraction measurements on a white neutron beam since the intensities (directly related to pole density) of many diffraction peaks (31 in this case) are determined with collinear diffraction vectors, that is along a single sample direction. Rietveld analysis, in particular, is key to the IPF determination, as the crystal-model based fit allows for accurate determination of pole density of orientations with significantly overlapped diffraction peaks. Thus, a single measurement on SMARTS, consisting of two diffraction patterns with orthogonal diffraction vectors, directly and

simultaneously measures two distinct IPF's along orthogonal directions, parallel and transverse to the straining direction.

C.2 Lattice Strains

Diffraction inherently selects grains with common crystal plane normals (poles) parallel to the diffraction vector (defined by the instrument geometry) and differentiates these based on interplanar (d-) spacing. For example, grains with their (110) poles parallel to the diffraction vector (and loading axis), so called (110) oriented grains, contribute uniquely to the diffraction peak at $d = 2.56 \text{ \AA}$ and said peak comprises an average response of this subset or family of grains. The change in the interplanar spacing along the different crystallographic directions as a function of applied stress, $d^{hkl}(\sigma)$,

represents elastic lattice strains,
$$\varepsilon_{lat}^{hkl}(\sigma) = \frac{d^{hkl}(\sigma) - d_0^{hkl}}{d_0^{hkl}},$$
 where d_0^{hkl} represents a reference interplanar spacing for the given crystallographic plane. A similar equation can be written with reference to the change in the individual lattice parameters, **a**, **b**, **c**. The statistical uncertainty associated with the Rietveld refinement of the lattice parameters is very small in all cases, typically on the order of 5×10^{-5} or less. In contrast, the uncertainty associated with single peak fits might be as high as 20×10^{-5} , in particular for broad peaks such as those from U-6Nb. These should be taken as relative uncertainties (or strain uncertainties) as absolute uncertainty is highly dependent on instrument calibration procedures and is, in all cases, significantly larger.

III. Experimental Results

A. Dependence on [Nb]

Neutron diffraction patterns from homogenized U-Nb samples with several different niobium concentrations are shown in figure 1. Each structure in the uranium-rich side of the phase diagram is represented. At the lowest niobium concentration studied, 0.25 wt%, the alloy is α' (orthorhombic). At a niobium concentration of 2.0 wt%, the crystallographic structure is still orthorhombic, but the peaks have shifted significantly and are considerably broader. The alloy is well into the α'' (monoclinic) phase field at a niobium concentration of 6 wt% and again, the peaks are very broad. Diffraction peaks indicative of both the α'' and γ^o (tetragonal) phases are observed in the 6.5 wt% alloy. At 7 wt% niobium, the diffraction peaks are once again sharp and the alloy is fully within the γ^o phase field. Finally, the high temperature body centered cubic phase, γ , is maintained to room temperature at a 10 wt% niobium concentration.

Figure 2 shows the behavior of the lattice parameters (**a**, **b**, **c** and γ) of the α' and α'' phases as a function of niobium content up to 6.25 wt%. The **a** lattice parameter increases with increasing niobium content while **b** decreases. Also, the **c** parameter increases weakly initially, but begins to decrease above 5 wt%. These trends are consistent with those published by Jackson [10] and Anagnostidis et al. [4], but differ from those reported by Tangri et al. [11]. Jackson [10] rationalized the behavior of the lattice parameters with increasing niobium content through a simple argument based on the relative sizes of the niobium and (highly anisotropic) uranium atoms. The rates of change of the α'' lattice parameters (**a**, **b**, **c** and γ) with [Nb] near 6 wt% in both an absolute and relative sense are shown in table 2. The **a** and γ parameters are the most sensitive to the niobium concentration, changing by 1 to 2% per unit change in [Nb]. The **c** lattice parameter is relative insensitive to [Nb] near 6 wt%.

Diffraction patterns were also collected from homogenized U-Nb alloy samples with [Nb] from 6.5-10 wt% in the γ_0 and γ phase. Though not reported fully here, it is worthwhile noting the lattice parameters of the γ_0 at the phase boundary of nominally U-6.5%Nb, are $a_{\gamma_0} = 4.935 \text{ \AA}$ and $c_{\gamma_0} = 3.365 \text{ \AA}$. These can be transformed into the α'' coordinate system to calculate corresponding values of $a_{\alpha''}$, $b_{\alpha''}$, $c_{\alpha''}$, and the monoclinic angle, γ , [36] as $2.986 \text{ \AA}$, $5.618 \text{ \AA}$, $4.935 \text{ \AA}$ and 98.22° . At 6.25 wt% Nb, the highest [Nb] shown in figure 2, the α'' lattice parameters are $2.914 \text{ \AA}$, $5.718 \text{ \AA}$, $4.965 \text{ \AA}$ and 93.26° . When compared to the evolution of lattice parameters with [Nb], it is clear that while the c lattice parameter changes little across the phase boundary, there is a discontinuous change in the a , b and γ lattice parameters across the boundary. Carpenter et al. [36] reported a similar discontinuous change when the phase transformation was driven in the reverse direction from γ_0 to α'' through application of stress.

B. Isothermal aging

Figure 3 shows diffraction patterns from homogenized U-6Nb material, immediately after reaching 473 K, 36 hours after reaching 473 K, and at room temperature after completion of the aging experiment. The diffraction patterns collected at elevated temperature have been offset from the other two for ease of comparison of the common temperature data. The first pattern collected at 473 K has relatively poor statistics because it was expected that the kinetics would be relatively fast immediately upon reaching temperature, so the integration time was short (~3 minutes) to optimize time resolution. The diffraction patterns have all been normalized to the integrated beam current during the individual runs, but are otherwise raw data. Clearly the diffraction pattern evolves strongly during the heating. The $(\bar{1}11)$ and $(\bar{1}10)$ peaks shift

significantly to higher d-spacing; the (110) shifts to a lesser degree to lower d-spacing. Continued evolution of the diffraction pattern is evident with extended time at temperature. In general, the peaks relax back toward their room temperature positions. Surprisingly, following cooling to room temperature, the diffraction pattern is indistinguishable from the initial room temperature diffraction pattern. The data were plotted in this way specifically to highlight the similarity between the room temperature diffraction patterns before and after 36 hours at 473 K.

Figure 4a shows the room temperature diffraction pattern from homogenized U-6Nb prior to heating. Figures 4b-d show (b) the initial pattern upon reaching 573 K, (c) after 1 hour and (d) after 35 hours at 573 K, respectively. Upon reaching 573 K, the material has transformed to the γ_0 phase. After an hour, the diffraction pattern is impossible to analyze quantitatively, but it appears that the material has reversed the transformation toward a two-phase α'' and γ_0 microstructure. After 35 hours, the diffraction pattern has continued to evolve, apparently towards the α'' structure, but again quantitative analysis is not possible.

Figures 5a-d show the evolution of the lattice parameters **a**, **b**, **c**, and γ of U-6Nb as a function of time at temperature following heating to a specified temperature (373 K, 473 K, and 523 K). Time zero is taken as the point at which the aging temperature is reached. The axes on the right of the plots show the fractional change in **a**, **b**, and **c** (the “lattice strain”), referenced to the value at room temperature prior to heating. The scales on plots a-c all represent 2.5% strain full scale. Like the sample heated to 573 K, the sample heated to 523 K partially transformed to γ_0 upon reaching the aging temperature, but was recognizably α'' within 10 minutes after reaching the target temperature. Thus,

the lattice evolution for this sample is shown starting 10 minutes after reaching temperature.

The initial changes in the lattice parameters of the homogenized U-6Nb with heating (over roughly 30 minutes) are strongly orientation dependent. The **a** lattice parameter increases dramatically with increasing temperature ($>2\%$ with $\Delta T \sim 170\text{K}$), while the **b** parameter decreases by roughly half that. The change in the **c** parameter is nearly within uncertainty of zero. The monoclinic angle, γ , increases strongly with increasing temperature. If the changes in lattice parameter are interpreted as thermal expansion, orientation dependent coefficients of thermal expansion may be determined and are shown in table 3, along with those of α uranium for comparison; they differ greatly. The thermal expansion coefficient of randomly textured U-6Nb is $14.5 \times 10^{-6}/\text{K}$ [14, 37], similar to that of α uranium, $13.9 \times 10^{-6}/\text{K}$ [38].

After the aging temperature is reached and the sample temperature is held constant, the lattice parameters evolve in the opposite direction (relax) relative to heating. The relaxation rate is temperature dependent; little relaxation is observed during the hold at 373 K, while the most rapid initial relaxation is observed at 523 K. With long times at temperature, the lattice parameters approach steady state values that are relatively independent of the aging temperature. The **a** lattice parameter decreases by more than 1% with 40 hours at 473 K and, regardless of temperature, approaches $2.923 \text{ \AA}$ at long times. The **b** lattice parameter increases with time at temperature such that by the end of the aging, the lattice parameter is nearly the same as the initial value at room temperature. The monoclinic angle decreases with time, asymptotically approaching 93.3° , roughly independent of the temperature.

With subsequent cooling to room temperature, much, if not all, of the lattice parameter evolution during the hold at temperature is recovered. That is, the final lattice parameters at room temperature after aging are similar to the fresh material, within 0.2%. After cooling from aging at 473 K to room temperature, the changes in the **a**, **b**, **c**, and γ lattice parameters relative to the as-quenched values are 0.07%, -0.04%, -0.1%, and 0.08° where uncertainties are typically roughly 0.02% . Likewise, after cooling from 523 K where partial transformation to the γ_0 -phase was observed on initial heating, the changes in the lattice parameters were -0.1%, -0.006%, -0.2%, and -0.01° at room temperature. Once again, effective orientation dependent CTE's can be calculated from cooling and are also shown in table 3. The CTE's on cooling are much closer to, although still distinct from, α -uranium.

Figure 6 shows the evolution of the fractional change in interplanar spacing of the $(\bar{1}10)$, (110) and $(\bar{1}11)$ planes, as well as the $(002)/(021)$ doublet during aging at 473 K. In order to compare with the Rietveld results, the same values were calculated using the **a**, **b**, **c** and γ lattice parameters. The single orientation (hkl) responses are well reproduced by the calculation based on the evolution of the lattice parameters. Interestingly, the $(002)/(021)$ doublet is also well captured by the average response of the two orientations calculated from the lattice parameters. This provides confidence in the interpretation of the results from the Rietveld refinement. Moreover, it provides an example of an even larger lattice strain response to the initial heating compared to that observed in the lattice parameters, with the $(\bar{1}10)$ and $(\bar{1}11)$ interplanar spacings increasing by more than 3% and 2.5%, respectively, when heated from room temperature to 473 K ($\Delta T \sim 170$ K). Again, the lattice strain relaxes with time at temperature and, like

the lattice parameters, return to within $\sim 0.1\%$ of their initial values when returned to room temperature.

While not shown for brevity, the peak breadths were also tracked during the aging heat treatment. The initial full width at half maximum ($\Delta d/d$) of the $(\bar{1}10)$, (110) and $(\bar{1}11)$ peaks are initially between 1% and 2% and do not change during the 473 K aging heat treatment outside of the uncertainty of 0.1% or less (depending on (hkl)).

C. Effect of Aging on Mechanical Properties

Figure 7 shows diffraction patterns collected at room temperature from the three tensile specimens made from banded U-6Nb material (offset for clarity): as-quenched and after 2 hours or 8 hours at 473 K. Based on the results shown in Fig. 5, it is unsurprising that other than a small peak at 2.03 Å from the steel blade of the extensometer in the 8 hour aged sample, the diffraction patterns are nearly identical. Lattice parameters determined from Rietveld refinement of the patterns are within the uncertainty that results from slight misalignment of the distinct samples in the load frame.

Figure 8 shows the stress-strain curves obtained from the three materials with different aging treatments. The dips in the stress-strain curves are due to relaxation while the test is interrupted to allow time to collect neutron diffraction data of sufficient statistical quality. The unloading data is not shown for the case of the as-quenched and 8 hour aged material because it obscures the figure without adding any new information. While it is clear that the initial yield point increases with aging at 473 K, accurate yield points are difficult to discern because the initial loading is never truly linear. However, taking the previously reported elastic modulus of 62 GPa [17], 0.2% offset yield strengths

are determined roughly to be 110 MPa for the as-quenched material, 350 MPa for the 2 hour aged material, and 440 MPa for the 8 hour aged material.

As is typical in U-6Nb, the initial yield point and region of reduced hardening rate is followed by increased hardening and a secondary yield point regardless of aging heat treatment. The secondary yield point (roughly marked by dashed lines) is chosen qualitatively as the point where the hardening rate is decreasing the most rapidly, at a strain of roughly 0.06. So defined, the secondary yield point occurred at stresses of 700 MPa in the as-quenched material, 730 MPa in the 2 hour aged material and 780 MPa in the 8 hour aged material. In contrast to the primary yield point, the dependence of the secondary yield point on aging is relatively small, occurring over a stress range of ~80 MPa. The difference in flow stress is roughly maintained throughout the remainder of the test. The current results show less age hardening associated with the secondary yield point than previously observed in low temperature aged material [23].

Figure 9 shows inverse pole figures parallel to the straining direction from the as-quenched and age heat treated materials at the start of the tensile test and after true strains of roughly 0.04, 0.08, and 0.12. Figure 10 shows the development of the (130) and $(\bar{1}30)$ pole densities, which effectively characterize the evolving texture, as a function of strain during tensile deformation of the as-quenched, 2 hour and 8 hour age heat treated materials. The initial yield points determined from figure 8 are represented by the dotted lines. The secondary yield point occurs at a strain of roughly 0.06. Prior to deformation, the texture of the material nearly random, regardless of heat treatment. The evolution of the texture with strain is relatively independent of the aging, with the as-quenched material exhibiting slightly stronger textures at the extreme points. In contrast, figure 11

shows the evolution of the same texture components as a function applied stress. Again, the dotted lines indicate the initial yield point defined for each material age in figure 8. The stress at which the initial increase of the (130) pole density occurs (100-500 MPa) depends strongly on the aging conditions and corresponds with the macroscopic initial yield strength. The secondary yield points occur between 700 MPa and 800MPa and roughly correspond to the maxima in the $(\bar{1}30)$ pole density.

IV. Discussion

To summarize the observations and ease the discussion, the stresses and strains at which various macroscopic phenomenon (e.g. primary yield) and diffraction effects (e.g. increase in (130) pole density) were observed are listed in table 4. Clearly, low temperature aging (i.e. at 473 K) has a pronounced effect on the mechanical response of U-6Nb, as well as the underlying micro-mechanics of the deformation. In as-quenched U-6Nb, the immediate increase of (130) pole density with strain (figure 10) parallel to the straining direction is due to preferential selection of specific martensitic variants that best accommodate the imposed deformation by motion of existing transformation twin boundaries (de-twinning) [17, 19, 39]. The point at which the (130) pole density reaches its maximum, at ~ 0.04 strain, marks the crossover from de-twinning to secondary mechanical twinning [18], manifested by a discrete re-orientation from the (130) to $(\bar{1}30)$ orientation, and corresponds roughly to the point where the macroscopic hardening rate, $d\sigma/d\varepsilon$, goes from increasing to decreasing. Subsequently, a strong $(\bar{1}30)$ texture component develops, reaching a maximum at ~ 0.09 strain, corresponding roughly to the second increase in macroscopic hardening rate. Finally, continuous rotation of the

texture component towards an (010) orientation, evident in the IPF's, signals the onset of dislocation mediated deformation at larger strains [18], appearing in figure 10 as a decrease in the $(\bar{1}30)$ pole density beyond roughly 0.09 strain.

The evolution of texture, which is indicative of the active deformation mechanisms, is nearly independent of the aging condition, meaning that the mechanisms that accommodate the enforced deformation do not change with the aging heat treatment. However, the stress necessary to initiate the deformation mechanism does change with aging heat treatment. In particular the motion of the pre-existing transformation twin boundaries, which is the dominant active deformation mechanism at small strains, becomes more difficult following the aging heat treatments. The initiation of de-twinning occurs at roughly 110 MPa in fresh material, 350MPa in the two hour aged material, and 440 MPa in the 8 hour aged material. In contrast, the crossover from de-twinning to the secondary twin, marked by the decrease in (130) pole density is only weakly dependent on the length of the aging heat treatment, occurring between 550-650 MPa. Moreover, the cessation of secondary twinning and activation of slip systems, indicated by the subsequent decrease in the $(\bar{1}30)$ pole density, is also only weakly dependent on the length of the aging heat treatment.

Thus, we conclude that while the active deformation mechanisms remain unaffected by aging, the initial yield point is increased because motion of the twin boundaries that form during quenching through the martensitic transformation requires an increased driving stress following aging. In contrast, the onset of secondary twinning and, subsequently, dislocation mediated plasticity are relatively unaffected by low temperature aging.

It is clear from the in-situ neutron diffraction data that the microstructure evolves during aging at 473 K. With initial heating, there is a pronounced transient response observed in lattice parameter that relaxes with time at temperature before fully recovering to pre-aging values when the sample is returned to room temperature. The large changes in lattice parameter with initial heating are not consistent with the thermal expansion of pure α -U and, moreover, are a transient response. Large, strongly anisotropic thermal expansion has been reported in other martensites that exhibit the shape memory effect [40], but no attempt was made to understand the source of the observation.

The aging temperatures discussed in this work (373 K, 473 K, 523 K and 573 K) are very near the austenitic transformation temperatures determined for this alloy. Hackenberg et al. report A_s and A_f temperatures of 444K and 485K, respectively, for U-5.75Nb when heated at ~ 50 K/sec [14]. These transition temperatures, in particular the A_s temperature, are somewhat higher than those reported by Vandermeer [9] who also showed that A_s increases with decreased heating rate. In the present work, we directly observe at least partial transition to the γ_0 phase when heating in-situ to 523 K and 573 K, but not 373 K or 473 K at much slower rates, ~ 0.1 K/sec. However, it is clear that the low temperature aging reported herein is near the austenite transition.

The large changes observed in the U-6Nb lattice parameters as the material is heated toward the austenite phase boundary are in the direction that is required by the structural phase transformation (i.e. $\alpha'' \rightarrow \gamma_0$) and are roughly the same magnitude. Carpenter et al. [36] reported a 2.1% decrease in the **a** lattice parameter, 3.4% increase in the **b** lattice parameter, and 3.7% decrease in the monoclinic angle (γ) relative to the equivalent spacings in the γ_0 phase when the phase transformation was driven from the γ_0

phase to the α'' phase by the application of stress. In this work, we observe a 2.5% increase in **a**, 1.7% decrease in **b**, and 5.0% increase in the monoclinic angle when crossing the boundary from α'' to γ_0 (i.e. the opposite direction from [36]) by increasing [Nb]. For comparison, when heating from α'' toward the γ_0 phase, we observe a 2% increase in **a**, 1% decrease in **b** and 3% increase in monoclinic angle. Thus, it appears as if the martensitic structure is “anticipating” the transformation to austenite as the transformation temperature is approached.

Based on the changes in lattice parameter across the phase boundary at room temperature with increasing niobium concentration, the transformation strains (α'' to γ_0) along any given crystal orientation have been calculated and are shown in figure 12a on the irreducible stereograph of the monoclinic structure. The dots represent the 31 distinct crystal orientations (hkl) at which the transformation strain was calculated to draw the contours (the same as the peaks included in the Rietveld refinement). As figure 6 demonstrates, the lattice parameter (**a**, **b**, **c**, and γ) changes observed during heating can be used to calculate the thermal strains at those same crystal orientations. Figures 12b and c show the thermal strains observed at the first time interval upon heating to 473 K and 373 K for the aging heat treatments, respectively. Both show the same trend over the stereograph as the transformation strains, supporting the idea that the lattice parameters are responding to move the structure toward the austenite phase, prior to reaching the transformation temperature. It is worth noting that the thermal strains can be calculated using the orientation dependent CTE of orthorhombic uranium and, after increasing temperature by 200K, the strains would be less than the single 0.5% contour interval on the scale of figure 12.

The relaxation of the lattice parameters with time at temperature is very large, $>1\%$, but could potentially be related to mechanical relaxation of internal stresses. In-situ diffraction studies have reported elastic lattice strains of this order during deformation of U-6Nb [17, 18] and even larger during stress induced phase transformation of γ_0 U-7Nb to α'' [33].

It is important to recall that a single diffraction peak comprises the response of many grains (in this case, martensite orientation variants) sharing a common orientation defined by a specific plane normal (hkl) parallel to the diffraction vector. While each individual grain sits in a unique neighborhood, the diffraction peak can be considered to represent the response of a single grain/variant in an average neighborhood, termed a Homogenous Equivalent Medium (HEM) in the parlance of self-consistent polycrystalline plasticity models [41, 42]. The HEM necessarily has the thermal (expansion) and elastic (stiffness) properties of the bulk material.

With this in mind, the observed data suggests the following. With increasing temperature approaching the austenite transformation regime, the lattice parameters evolve strongly and anisotropically in anticipation of the transformation; the effective CTE along the $(\bar{1}10)$ plane normal is over $170 \times 10^{-6}/\text{K}$. Randomly textured U-6Nb has a macroscopic CTE of $\sim 14.6 \times 10^{-6}/\text{K}$ [14, 37] at room temperature. Large intergranular/intervariant stresses develop due to the constraint of the neighborhood. For example, Clarke et al. [39] reported the presence of some intergranular tensile accommodation strains after deformation in compression, even though negative accommodation strains were determined for the majority of the martensite variants within the grain. With time at temperature, these stresses relax.

The response of the grains/variants is phenomenologically analogous to a “stress relaxation” test [43-45], in which a macroscopic increment of displacement is imparted to the boundaries of a mechanical test specimen, resulting in a corresponding instantaneous increase in stress. Subsequently, the crosshead displacement is held constant and the decrease in stress on the sample is monitored with time. Empirically, the time

dependence of the stress decrease follows the form $\Delta\sigma = \sigma(t) - \sigma_0 = \frac{-kT}{V} \log\left(1 + \frac{t}{\tau}\right)$,

(sometimes called the Feltham equation) where V represents an activation volume, τ is a characteristic relaxation time, k is the Boltzmann constant and T the temperature [44-46].

In the analogy with the U-6Nb grain/variant in a polycrystalline matrix, the incremental displacement of the grain is provided by the large directional thermal expansion of the grain relative to the isotropic surrounding HEM. Subsequently, as the temperature (displacement) is held fixed, the stress relaxes in the grain and the HEM plays the constraining role of the fixed loading machine. The stress on the grain is necessarily proportional (in a tensor sense) to the elastic portion of the strain which is observed by diffraction, $\sigma_{ij} = C_{ijkl}\epsilon_{kl}$ where C_{ijkl} represents the single crystal stiffness tensor. For the purposes of this rough analogy, we will simply consider a scalar approximation of Hooke’s Law, $\sigma = E_{hkl}\epsilon$, where E_{hkl} is the effective elastic modulus along the specific crystal direction. With this simplification, the Feltham equation can

then be written as $\Delta\epsilon_{hkl} = \frac{-kT}{VE_{hkl}} \log\left(1 + \frac{t}{\tau}\right)$ and related directly to the elastic strains

observed by diffraction while holding at temperature.

Figure 13a shows the relaxation of the elastic strains ($-|\Delta\epsilon|$) after heating to 473 K determined from the lattice parameters, **a**, **b**, **c**, and γ (shear strain calculated from the

change in the monoclinic angle) fit to the Feltham equation. Figure 13b shows the same for specific crystallographic orientations, $(\bar{1}10)$, (110) , and $(\bar{1}11)$. The fits are excellent. The characteristic times, τ , derived from the fits are dependent on the orientation, but are on the order of minutes. Likewise, the activation volumes, V , are on the order $13000 \text{ \AA}^3$, corresponding a length of $\sim 20 \text{ \AA}$, or of order 5 unit cells.

It must be stressed that this is a simplistic analogy. The stress relaxation test is defined as uniaxial, while the distortion and constraint on a grain in a polycrystal is inherently triaxial. Moreover, the “displacement” is not held fixed as the grain/variant and surrounding neighborhood relax. The evolution of the strain with time can be fit nearly as well with a power law, i.e. corresponding to a creep test. However, given the simplicity of the analogy, the derived results are reasonable and provide confidence in the rationalization of the observations.

Following low temperature aging, the initial yield stress of the banded U-6Nb is observed to increase due to the increased resistance to motion of the transformation twin boundaries formed during the quench to room temperature (Fig. 11). Clarke et al. [23] speculated that this might be due to rearrangement of transformation twin/lath interfacial structures into lower energy configurations by viscous glide, climb, or ledge/step migration. The thermoelastic martensite structure formed during a rapid quench from the solutionizing temperature of 1073 K consists of multiple variants with twin and near-twin orientation relationships between them [20]. Defects within these interfaces (likely complexes of transformation dislocations, ledges, step, and disconnections [47]) are necessarily mobile in order to both effect the initial transformation and allow relatively easy interface migration (“de-twinning”) during shape memory deformation. However,

these interfacial defects are not likely to be in their lowest energy configurations due to the rapid quench. Low temperature aging provides both additional energy in the form of the elevated temperature and a strong driver in the form of large intervariant stresses for rearrangement of the variant interfaces to lower energy, less mobile states, with concomitant increased resistance to motion, resulting in the increased initial yield stress. These interfacial rearrangements would also be expected to partially stabilize the martensite structure, resulting in the observed increases in A_s and A_f temperatures with low temperature aging [9] and reverse transformation during aging at 523 K and 573K observed in this work.

The authors are not aware of any previous proposal of such a mechanism for aging in a SME system. The current diffraction data is unable to provide validation of this speculation as it is unlikely that such local rearrangements would produce an easily recognizable signature in the diffraction measurement which averages over cubic millimeters. However, the current results are consistent with the proposed aging mechanism, thus providing some support. A combination of modeling, using methods such as those in [47, 48], and high resolution TEM would be required to address this hypothesis. This would be a challenging undertaking, given the complexity of the crystallography for the martensitic transformation in this system and the high atomic number of uranium which makes high resolution TEM particularly difficult.

While the current data cannot provide direct proof of the age hardening mechanism, it can be used to exclude other potential low temperature aging mechanisms. The slow evolution of the lattice parameter with time was originally suggested to be associated with a decrease in niobium concentration [14] by phase separation, as is

unambiguously observed in higher temperature aging [8, 9, 21-25]. However, this was later realized to be implausible, as the lattice parameters return to their original room temperature values upon cooling to room temperature, to within 0.2%. Atom probe tomography after low temperature aging at 473 K also did not reveal significant compositional variations indicative of phase separation [23]. Indeed, the actual relative changes observed in the lattice parameter are not consistent with changes in niobium concentration, as the largest change in lattice parameter observed at room temperature before and after the aging heat treatment is in the *c* parameter, which is almost independent of niobium concentration (see Fig. 2c). From figure 2, it is apparent that near 6 weight percent niobium, the *a* and γ parameters are most sensitive to changes in niobium concentration. The largest observed change in the *a* parameter, -0.1%, after aging at 523 K would correspond to a decrease of ~0.1 weight percent of niobium. Likewise, the largest change in γ angle of 0.08° after aging at 473 K corresponds to a decrease of less than 0.05 weight percent niobium. These could be taken as upper limits to the amount of phase decomposition observed during the aging heat treatment.

Another potential low temperature aging mechanism is spinodal decomposition of the U-Nb alloy [26]. Periodic modulation of the niobium content on nanometer length scales associated with spinodal decomposition would not necessarily result in a change in the bulk averaged lattice parameter, but rather an increase in peak breadth corresponding to the distribution of niobium concentration. Given the uncertainty in the measurement of the peak FWHM, roughly 0.1%, the measurement should be sensitive to a similar distribution of lattice parameters, which corresponds to amplitude in the modulation of the niobium content of roughly 0.2 weight percent. In other words, the observed lack of

peak broadening puts an upper bound on niobium content modulation due to spinodal decomposition of 0.2 weight percent.

V. Conclusions

In-situ neutron diffraction measurements during and aging heat treatment and deformation of 473K aged nominally U-6Nb materials were completed in an attempt to understand the microstructural origin of the reported increased strength of material following aging heat treatments. At the initial low-stress yield point of U-6Nb, strain is accommodated by preferential selection of specific martensitic variants through motion of transformation twins formed during quenching through the martensitic transformation [17] [19, 39]. An increased driving stress to move the twin boundaries is responsible for the observed increased flow stress.

Unfortunately, the diffraction measurements completed in-situ during low temperature aging do not provide a clear cause for the increase resistance to motion of the twin boundaries. With initial heating, large anisotropic transient changes in the monoclinic lattice parameters are observed, followed by subsequent relaxation with time at constant temperature. The response is well described by considering the martensite variant microstructure as individual anisotropic “grains” in an isotropic effect medium. With heating, the grains expand/contract depending on crystal orientation against the constraint of the surrounding medium setting up a large stress, which relaxes with time. The observed relaxation of the elastic lattice strains is well fit by the Feltham equation, which has been developed to fit stress relaxation tests [44, 49, 50].

Upon return to room temperature, the lattice parameters return to their pre-aging values. Virtually no change in the diffraction pattern is observed when comparing before

and after aging. This result is consistent with a previous suggestion of strengthening due to rearrangement of twin interface structure during aging [23], but cannot provide direct evidence, as it would not present an unambiguous signature in the diffraction data. The current neutron diffraction data can exclude other possible aging mechanisms, such as phase separation by either nucleation and growth or spinodal decomposition, which should be manifested by easily observable permanent changes in the lattice parameters and/or peak breadths, which are unambiguously not observed.

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Tables

	Nb	C	Cu	Fe	Al	Si	Mo	Ti
Homogenized Material	6.04	0.0002	5E-5	0.0004	1e-5	0.0003	3E-5	1E-5
Banded Material	5.77	0.020	0.0044	0.029	0.003	0.026	0.0048	0.0016

Table 1. Sample impurity concentrations in wt%.

	a	b	c	γ
Units of Å/wt%Nb	0.029	-0.037	-0.018	1.8°
Units of %/wt%Nb	1.0	-0.6	-0.3	2

Table 2. Rate of change of the α'' lattice parameters with change in Nb concentration near 6 wt%Nb in absolute (Å/wt%Nb) and relative (%/wt%Nb) units.

	a	b	c
α -Uranium	27	-1.6	24
U-6Nb heating	120	-48	-5
U-6Nb cooling	54	-5	11

Table 3. Effective single crystal CTE's (units of $10^{-6}/\text{K}$) of U-6Nb alloys and pure α -uranium [38].

Observation	As-quenched	2hr 473C	8hr 473C
Primary yield point	110 (0.003)	350 (0.007)	440 (0.009)
Increase of (130) pole density	110 (0.002)	360 (0.004)	450 (0.004)
Secondary yield point	700 (0.06)	730 (0.06)	780 (0.06)
Maximum in (130) pole density	484 (0.041)	607 (0.042)	653 (0.042)
Minima in ($\bar{1}$ 30) pole density	285 (0.021)	410 (0.023)	503 (0.023)
Maximum in ($\bar{1}$ 30) pole density	770 (0.087)	781 (0.093)	N/A

Table 4. Stress (MPa) and strain (in parenthesis) at which various macroscopic and microscopic phenomenon were observed.

Figure 1. Diffraction patterns from several uranium-niobium alloys after quenching from the high temperature γ phase. The upper and lower tick marks in the U6.5Nb pattern represent the peaks associated with the α'' and γ_0 phases, respectively.

Figure 2. Lattice parameters of as-quenched uranium-niobium alloys as a function of niobium concentrations (from chemical analysis). Open and closed symbols represent data taken in the 2 banks on the NPD.

Figure 3. Diffraction patterns from as-quenched homogenized U-6Nb material, immediately upon reaching 473K, 36 hours after reaching 473K, and after returning to room temperature. The elevated temperature patterns are offset to allow for easier comparisons of patterns collected at like temperatures. Reflections that are relevant to the discussion are indexed.

Figure 4. Diffraction patterns from homogenized U-6Nb in the (a.) as-quenched condition, (b.) immediately after rapid heating to 573K, (c.) 1 hour after reaching 573K, and (d.) 35 hours after reaching 573K.

Figure 5. Evolution of the U-6Nb lattice parameters (a, b, c, g) with time at temperature. The axes on the right indicates the relative change (strain), and all represent 2.5% full scale. Every 20th data point is represented by a symbol.

Figure 6. Evolution of the lattice strains of the $(\bar{1}10)$, (110) and $(\bar{1}11)$ peaks as well as the $(002)/(021)$ doublet (symbols). The lines represent the same strains calculated from the lattice parameters found by Rietveld refinement.

Figure 7. Room temperature diffraction patterns from banded U-6Nb tensile samples in the as-quenched condition as well as after 2 and 8 hours at 473 K.

Figure 8. Stress/strain curves for as-quenched banded U-6Nb as well as material aged 2 and 8 hours at 473K. The dotted and dashed lines represent the approximate initial and secondary yield points, respectively.

Figure 9. IPF's representing texture evolution of the as-quenched and aged U-6Nb at true strains of roughly 0, 0.04, 0.08, and 0.12.

Figure 10. Evolution of the (130) (closed symbols) and $(\bar{1}30)$ (open symbols) pole densities as a function of tensile strain.

Figure 11. Evolution of the (130) (closed symbols) and $(\bar{1}30)$ (open symbols) pole densities as a function of applied stress. The dotted and dashed lines represent the primary and secondary yield points gleaned from Fig. 8.

Figure 12. a.) Transformation strains (α'' - γ^0) calculated from lattice parameters given in [36] when the reverse transformation was driven by deformation. b.) and c.) Strains observed by diffraction when heating homogenized U-6Nb to 473 K and 373 K,

respectively. Contours range from -6.5% to 6.5% at intervals of 0.5%. The thick line marks 0.

Figure 13. Observed (solid circles) strain relaxation ($-|\Delta\varepsilon|$) in a.) lattice parameters and b.) specific single peaks during hold at 473 K fit with the Feltham equation (solid lines).

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Figure 13. Observed (solid circles) strain relaxation ($-|\Delta\epsilon|$) in (a.) lattice parameters and (b.) specific single peaks during hold at 473K fit with the Feltham equation (solid lines).

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