The influence of impurities on the crystal structure and mechanical properties of additive manufactured U-14 at.% Nb

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Abstract

Uranium-niobium alloys can exist with significantly different microstructures and mechanical properties, heavily influenced by thermomechanical processing history and impurities. Here, the influence of Ti and other impurities is studied on uranium-14 at.% niobium additively manufactured using laser powder bed fusion. Two different metallic impurity levels were investigated and a Nb equivalent (Nb_{eq}) composition is defined to represent the impurities. *In-situ* neutron diffraction during compression loading shows that increased Nb_{eq} promotes the formation of γ^0 -tetragonal phase at the expense of α'' -monoclinic phase, resulting in 2x higher yield strength than water quenched α'' and a strain induced transformation to α'' with superelastic strains to 4.5%.

Keywords: Additive manufacturing, laser powder processing, neutron diffraction, superelasticity, martensitic phase transformations

Article

Due to their attractive mechanical properties, high densities and unique nuclear properties, uranium alloys comprise the majority of nuclear fuels. For these applications, alloying with Nb, Ti, Mo, V, Ta, etc. can be desirable for enhanced ductility and corrosion resistance. However, even small alloying additions and/or impurities can lead to significant and highly process dependent differences in thermal and mechanical behavior of these alloys. Low concentration alloys with the α -phase (orthorhombic) structure are used chiefly in thermal nuclear reactors, while higher alloys with a γ -phase (bcc) structure can provide enhanced thermal volumetric stability and corrosion resistance [1].

U-6Nb is a metastable alloy that is most often produced with a microstructure that forms martensitically during rapid cooling from γ_1 (bcc) to α'' (monoclinic), but can also contain γ^0 (tetragonal) in high Nb regions of the microstructure [2]. In this study, the microstructure-property behaviors of two U-6Nb alloys with different impurity levels that were fabricated using laser powder bed based additive manufacturing (AM) are investigated. Laser powder bed AM provides the means for directly fabricating components from fine powders with near net-shape, fine-featured, complex geometries, and with high material usage efficiency which is important for many applications. This process builds components using small overlapping laser melt pools at high speeds,

resulting in high solidification rates and correspondingly refined microstructures compared to traditional castings [3]. The refined AM microstructures produce less chemical segregation, or banding [2], which corresponds to faster homogenization (Fig. S1) and more uniform mechanical properties on the microstructural scale. The two powder alloys investigated here differ in composition such that one alloy contains a significantly higher amount of Ti than the other, and will be referred to as the high impurity alloy. AM parts made from both alloys were characterized using neutron diffraction and compression testing in order to identify the influence of impurities on AM fabricated U-6Nb components.

Chemical analysis was performed on the initial powders and also on the AM parts made from these powders (Table 1). The results show that the major difference in the alloys is the Ti content, which measures 2.37 at.% (0.49 wt.%) in powder 1 (high impurity), and 0.0022 at.% (0.00044 wt.%) in powder 2 (low impurity). In addition, Mo and V are notably different in the two powders, whereas other impurity differences exist but on a smaller scale (see Supplementary Information for a complete list of impurities). Both alloys contain 13.6-13.9 at.% (5.9-6.0 wt.%) Nb, which is the only intentionally added element in this alloy. After fabrication, there are only minor changes in the impurity elements from the starting powder.

The AM parts were fabricated on a Concept Laser M2 powder bed system, using a 400 W NdYAG laser with a wavelength of 1064 nm focused to a 50 μm $D4\sigma$ Gaussian spot size. The beam was moved at speeds up to 1 m/s, and argon shielding gas was used to blow away the laser plume and protect the sample from excess oxidation. The starting powders were shown to have a mean diameter between 53 and 63 μm from sieve analysis and are described in detail elsewhere [4]. AM specimens were processed on cast U-6Nb build plates using island scanning where the laser beam is rastered back and forth in a 5 x 5 mm square and squares are randomly deposited, yielding a checker-board-like deposited layer with adjacent islands scanned orthogonally to each other [5]. It is known that residual stresses can be high in laser powder bed fusion builds [6], but can be reduced in this fashion with small scan vector length [7]. All mechanical specimens were built horizontally owing to limited powder quantities.

Similar to conventional U-6Nb, heat treating was performed to homogenize the as-built parts (Table 2). The high impurity samples were held at 1000 °C under medium vacuum (6-8 mTorr) for 10 hours, cooled to 840 °C for 30 min, then rapidly quenched by dropping the specimens into a water bath. Prior to mechanical testing, these samples were further aged at 200 °C for 2 hours. Neutron diffraction was performed on high impurity specimens both with and without aging (Fig. S2). The low impurity samples were also heat treated under medium vacuum and water quenched, but with no additional aging treatment. Neutron diffraction and *in-situ* compression testing was performed after the samples were homogenized for 1 hour at 1000 °C, cooled to 840 °C for 30 min, and water quenched. Mechanical characterization was performed on low impurity samples that were held at 1000 °C under medium vacuum for 16 hours, cooled to 840 °C for 30 min, and water quenched. Specimens possess a small amount of spherical porosity (<0.5% from immersion density). Their microstructures progress from overlapping weld pool passes with fine grains on the order of a few microns to equiaxed grains < 50 μm at the longest annealing times.

The compression test specimens were removed from the build plate via wire electro-discharge machining, and further lathe machined to a diameter of 5.7 mm with ends ground parallel to a length of 12.7 mm. Testing was performed in a screw-driven machine using displacement control at 0.01mm/s, which corresponds to a strain rate of 0.08/s on the sample as measured by a strain gage extensometer. Similar testing was performed during *in-situ* neutron diffraction on the SMARTS diffractometer at the Manuel Lujan Jr. Neutron Scattering Center, LANSCE, Los Alamos National Laboratory, with the added ability to directly evaluate crystal structures during compression testing. Details of the neutron diffraction facility and analysis are discussed elsewhere [8].

Neutron diffraction was used to measure phase fractions in the AM parts with a 2 mm³ interaction volume, which is considered to represent a statistical average over a large number of grains. Diffraction patterns were analyzed for phase fractions using a Rietveld analysis [9] on the starting powders, the as-built samples, and the post heat treated samples. Rietveld analysis was completed on the diffraction data using the General Structural Analysis System (GSAS) software package developed at Los Alamos [10]. For the α'' structure, 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 Nb concentration orthorhombic phase with the monoclinic phase at intermediate Nb concentrations, with the transformation being manifested by the deviation of the angle between the a and b lattice vectors from 90° [11]. For the γ^0 structure a P 4/n m m space group was utilized.

Neutron diffraction patterns are presented in Fig. 1 for the low and high impurity alloys in the different conditions, including the raw powders. Analysis of these diffraction peaks was performed to calculate the fraction γ^0 and α'' for each condition. Examples of the 100% γ^0 and of the nearly 100% α'' diffraction patterns are shown in Fig. 1F and Fig. 1c respectively. Note that all phase fractions are reported in wt.%. The results show that the U-6Nb builds made using the high impurity alloy possessed approximately 50% γ^0 / 50% α'' (Fig. 1e), which is similar to the phase fraction in the raw powder (Fig. 1d). After homogenization/WQ the high impurity alloy assumed a 100% γ^0 structure (Fig. 1f). The low impurity alloy showed 42% γ^0 / 58% α'' in the as-built condition (Fig. 1b), which is similar to the raw powder (Fig. 1a). After homogenization/WQ the low impurity alloy had approximately 100% α'' (Fig. 1c); this structure was not affected by aging at 200°C for 2 hours. The approximately 50% α'' monoclinic structure, observed in both the low and high impurity alloys in the as-built condition is different than wrought and cast U-6Nb subjected to post-processing homogenization heat treatments without water quenching [2,12]. Furthermore, the 100% γ^0 tetragonal structure after homogenization/WQ observed in the high impurity alloy would not be expected in conventional U-6Nb, and this difference is attributed to the high impurity content.

The U-Nb binary phase diagram [13], including metastable phases [2], is shown in Fig. 2. Under equilibrium conditions the room temperature microstructure of U-6Nb would be expected to be composed of α -U (orthorhombic) with essentially no Nb in solid solution, and γ_2 (bcc) that contains approximately 75 at.% (58.5 wt.%) Nb. Multiple variations of the α and γ phases are known to exist depending on the Nb content [2,14]. However, due to low diffusivity of Nb in U, equilibrium conditions are not achieved without extended heat

treating. Because of this, metastable phase variants of α and γ_2 , depending on the alloy content, form as indicated in Fig. 2 [2]. In this figure, corresponding paired lines represent the martensite start (M_S) and martensite finish (M_F) temperatures on cooling. Higher cooling rates favor martensitically formed metastable phases by avoiding diffusional decomposition of γ_1 during cooling to room temperature. It has been shown that cooling rates in excess of 20°C/s are required to avoid decomposition of γ_1 , which is easily achieved during water quenching [12]. However, the cooling rates, and the effects of subsequent reheating of the microstructure that occurs during AM processing are not known, nor are the effects of impurity elements on the phase transformations in U-6Nb.

The compositions of the two powder alloys are further plotted in Fig.2, showing their relationship to the metastable phases at room temperature. Two different compositions are plotted for the powders. The first is calculated from the Nb/(Nb+U) ratio, assuming all of the trace impurities can be neglected, which results in an effective Nb content of 14.1 at.% (6.0 wt.%) for both powders, and is indicated by “a” on the plot. The second method considers an equivalent Nb concentration (Nb_{eq}) whereby the bcc transition metal elements (Nb, V, Mo, etc.) plus Ti and Zr which are bcc at elevated temperatures, are combined as if they all behave like Nb, prior to taking the $Nb_{eq}/(Nb_{eq}+U)$ ratio where Nb_{eq} (at.%) = Nb+Ti+Mo+V+Ta+Zr+W. The rationale behind the Nb_{eq} calculation is that at elevated temperatures, either during the AM build or heat treating in the bcc γ_1 region, these elements would be in solid solution along with Nb in U, and during rapid cooling they may have a similar effect as Nb on the M_S and M_F temperatures during the γ_1 to α'' or γ^0 martensitic phase transformation. Note that at.% is used in the Nb_{eq} equation since an atom-to-atom replacement of Nb by the impurity elements would be expected to affect the M_S and M_F in a similar manner for substitutional alloying in the bcc γ_1 crystal structure prior to quenching. The calculated Nb and Nb_{eq} ratios show that the effective Nb content increases as the result of the metallic impurity elements from 14.1 at.% (6.0 wt.%) Nb when only Nb is considered, to 14.9 at.% (6.4 wt.%) Nb_{eq} in the low impurity alloy, and then to 16.7 at.% (7.3 wt.%) Nb_{eq} in the high impurity alloy. By considering the impurity elements, Nb_{eq} is increased such that it pushes the compositions from below the M_F in the α'' phase field for U-6Nb, to a value near the M_F for the low impurity alloy to “b”, and then above the M_S and into the γ^0 phase field for the high impurity alloy to “c”. Therefore, it should be possible to directly quench the high impurity alloy into the γ^0 phase at room temperature if the cooling rate is high enough, and that is exactly what is observed and shown by the neutron diffraction data in Fig. 2f when this alloy is water quenched from the γ_1 phase field.

Conventional U-6Nb alloys that have been rapidly cooled, or quenched, and have gone through martensitic phase transformations with high volume fractions α'' , display two stage yielding [2,15,16]. At low strains, up to about 5%, the α'' martensite detwins under strain, creating a lowered hardening rate, or stress plateau, in this strain range. At higher strains, slip dominates plastic deformation along with twinning [2], producing a second yield point and associated non-reversible plastic deformation [2,15,16,17]. The high impurity alloy however is nonconventional, having a lower fraction % α'' martensite (50 vs 58%) in the as-built condition, and is 100% γ^0 (0% α'') after homogenizing and water quenching. The different starting microstructure of the high impurity alloy has a major influence on its mechanical behavior.

Compression testing of the high impurity alloy in the homogenized/WQ/aged condition was performed during *in-situ* neutron diffraction to strains up to 8 %. These results are in Fig. 3, showing a first yield strength of 550 MPa, which is considerably stronger than conventional U-6Nb alloy when similarly aged for 100 min at 200°C (σ_y 250-400 MPa) [2]. Note that the small unloading deviations in the curve correspond to constant strain hold points where neutron diffraction data were taken. After yielding, there is a pronounced level portion of the curve before strain hardening increases at approximately 4.5% strain. Upon unloading from 8% strain the sample recovers approximately 3% plastic strain on unloading. Also plotted in Fig. 3 are the phase fractions of the *in-situ* diffraction results during compression testing showing the stress induced phase transformation from γ^0 to α'' . These observations confirm 100% γ^0 in the high impurity alloy starting condition, and it is clear that during compression the γ^0 tetragonal structure transforms to 100% α'' monoclinic at 6.0 % compressive strain. The open circles on this plot further show the phases that coexist during unloading of this sample, where the α'' phase partially transforms back to approximately 50% γ^0 with 3% plastic strain unrecovered when the load is completely removed.

Additional compression tests were performed using a conventional screw-driven testing machine to further study the reversible component of the low-strain plasticity in the high impurity γ^0 alloy. These tests were performed by compressing the sample to a predetermined peak strain and unloading to 0% strain, with three repeats for each strain cycle. The peak strain was then increased in 0.5% increments until non-reversible plastic deformation was observed. The results are shown in Fig. 4a, indicating fully reversible deformation up to 4.5% peak strain. It is clear that the stress spread of the hysteresis loop increases as the peak stress increases, requiring lower loads for the unloading curve to join the loading curve as the peak strain is increased. At peak strains larger than 5% some non-reversible plastic strain is observed, presumably as a result of slip and/or twinning becoming more active than martensite formation during compression [2,15,16]. The large reversible plastic strains, or superelasticity, observed in the high impurity alloy is the result of a martensitic phase transformation that occurs in U-Nb [2,12], and is related to a well-known shape memory effect in U-6Nb [17,18]. The superelastic strains, created by stress induced martensite formation can be completely recovered during unloading without heating as shown in Fig. 4a. In the case of the high impurity alloy, which quenches into the γ^0 structure, compression creates a stress induced transformation to martensitic α'' ; upon unloading the martensite transforms reversibly back to the γ^0 at low strains.

The mechanical behavior of the low impurity alloy after homogenization/WQ is substantially different. Fig. 4b shows the first three compression cycles of this alloy strained to a peak value of 2% each. Superimposed on this plot is a stress-strain curve for the same material tested to failure in compression in a separate sample. The 2% compression cycles show essentially no plastic strain recovery upon unloading. Subsequent cycles contribute to the total plastic strain such that the composite stress-strain behavior follows the one-cycle stress-strain curve to failure, and has a yield strength of 230 MPa. The plastic deformation that is observed at low strains in the low impurity alloy could only be recovered by heating the alloy above the M_s temperature and into the γ^0 phase field where α'' would transform back to the γ^0 phase through the shape memory

effect [17,18]. Neutron diffraction indicates that the low impurity materials starts in the α'' phase and shows no significant phase transformation during compressive deformation. Indeed, texture determinations made during the compression test indicates that the low impurity AM material behaves very similarly to conventional wrought U6.

Based on neutron diffraction it is clear that the small amounts of metallic impurities can significantly alter the microstructures of U-6Nb in both the as-built and heat treated conditions. It was shown that the alloy with low impurities of 2.1 at.%, principally Mo and V, is similar to conventional U-6Nb after homogenization/WQ where increased chemical homogeneity allowed the low impurity alloy to be quenched near its α'' M_F temperature to nearly 100% α'' . Increasing the impurity level to 3.1 at.%, (principally Ti and Mo, had a more dramatic effect whereby the as-built microstructure contained $\sim 50\%$ α'' in the microstructure. However, after homogenization/WQ this alloy transformed to 100% γ^o , which is significantly different than conventional U-6Nb alloys and is also significantly different than the low impurity alloy studied here.

Treating the bcc metallic impurity elements as if they have the same effect on metastable phase formation as Nb, allowed a Nb_{eq} to be calculated. The Nb_{eq} composition was shown to be above the α'' M_S at room temperature in the high impurity alloy, explaining its 100% γ^o microstructure after homogenization/WQ. The mechanical properties of these two alloys were affected by their different microstructures. *In-situ* neutron diffraction compression testing of the high impurity alloy showed much the same behavior in the as-built condition. However, after homogenization/WQ/aging, the high impurity alloy contained 100% γ^o and showed a yield strength increase of more than 2x over α'' , to 550 MPa, with superelastic behavior observed at strains up to 4.5%.

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Competing interest's statement

The authors declare that they have no competing financial interests.

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Table 1. Concentration of impurities in the U-6Nb powder and U-6Nb specimens after powder bed fusion processing measured via ICP-MS. The phase fractions for α'' (monoclinic) and γ^o (tetragonal) are indicated for each condition based on neutron diffraction. All compositions are in atomic ppm unless otherwise noted.

Element	Powder 1	As-built	HT/WQ	Powder 2	As-built	HT/WQ
Nb	136,000±1000	137,700±400	N/A	139,000±2000	138,400±300	N/A
Ti	23,700±300	23,200±300		22±2	26±3	
Mo	6,190±70	6,200±100		2,400±90	2,460±30	
Zr	247±5	277±5		166±4	206 ±4	
Ta	13.7±0.2	22.2±0.4		164±3	168±2	
V	4.6±0.3	5.8±0.2		8,100±100	8,000±200	
W	6.9±0.1	7.6±0.4		12.9±0.2	13.7±0.2	
Fe	210±20	190±20		3,260±90	3,500±200	
Al	310±20	330±10		5,800±300	6,400±400	
Ni	63±2	63±2		230±10	280±10	
Cu	44.8±0.7	44.2±0.7		367±8	340±20	
Mn	32.0±0.7	30.3±0.8		70±10	69±3	
O	<310 [†]	-		<310 [†]	-	
U (bal)	832,700	831,800		840,200	840,100	
Nb/(U+Nb)	14.1	14.2		14.2	14.1	
wt.%	(6.01)	(6.07)		(6.07)	(6.04)	
Nb _{eq} /(U+ Nb _{eq})	16.7	16.8		14.9	14.8	
wt.%	(7.27)	(7.31)		(6.41)	(6.37)	
wt.% α'' [‡]	36	50	0	42	58	~100
wt.% γ^o [‡]	64	50	100	58	42	~0

[†]From manufacturer; value in ppm weight

[‡]Neutron diffraction phase analyses are made within resolution of the acquired spectra

Table 2. Definition of heat treatments applied to the high and low impurity U-6Nb specimens

ND1	1000°C for 10 h, cooled to 840°C for 30 min, water-quench, aged at 200°C for 2 h
ND2	1000°C for 10 h, cooled to 840°C for 30 min, water-quench
ND3	1000°C for 1 h, cooled to 840°C for 30 min, water quench
TENS1	1000°C for 10 h, cooled to 840°C for 30 min, water-quench, aged at 200°C for 2 h
TENS2	1000°C for 16 h, cooled to 840°C for 30 min, water quench

Fig. 1. Diffraction patterns from U-6Nb for the low impurity alloy in: a) powder, b) as-built, and c) homogenized/WQ condition; compared with diffraction patterns for the high impurity alloy in the d) powder, e) as-built, and f) homogenized/WQ/aged condition.

Figure 2: U-Nb binary alloy phase diagram, developed by Thoma et al. and reproduced with permission from [2], with martensite start, M_s , and martensite finish, M_F , temperatures indicated for the metastable phases. Composition points are plotted (squares) at room temperature in the zoomed in region of the diagram indicating specific compositions “a” U-

6Nb assuming no impurity effect; “b” the low impurity alloy, and, “c” the high impurity alloy based on Nb_{eq} calculations.

Fig 3: Stress-strain plot to 8% peak strain in compression and corresponding γ^0 phase fraction for the high impurity alloy in the ND1 condition acquired during *in-situ* neutron diffraction.

Fig 4: a) Stress-strain curves on loading and unloading for the high impurity alloy in three consecutive cycles of 2% each, superimposed on the stress-strain curve to failure. b) Stress-strain curves on multiple cycle loading and unloading for the low impurity alloy, illustrating superelastic behavior to 4.5% strain.

Figure(s)

Figure 2

Figure 3

(a)

Figure(s)