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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°-tetragonal phase at the expense of α″-monoclinic phase, resulting in 2× higher yield strength than water quenched α″ and a strain induced transformation to α″ with superelastic strains to 4.5%.

1. Introduction

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° (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 D4σ 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

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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° (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	6190 ± 70	6200 ± 100		2400 ± 90	2460 ± 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		8100 ± 100	8000 ± 200	
W	6.9 ± 0.1	7.6 ± 0.4		12.9 ± 0.2	13.7 ± 0.2	
Fe	210 ± 20	190 ± 20		3260 ± 90	3500 ± 200	
Al	310 ± 20	330 ± 10		5800 ± 300	6400 ± 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[a]	–		<310[a]	–	
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}/(+ Nb_{eq})	16.7	16.8		14.9	14.8	
wt.%	(7.27)	(7.31)		(6.41)	(6.37)	
wt.% α″[b]	36	50	0	42	58	~100
wt.% γ°[b]	64	50	100	58	42	~0

[a] From manufacturer; value in ppm weight.
[b] Neutron diffraction phase analyses are made within resolution of the acquired spectra.

island scanning where the laser beam is rastered back and forth in a 5 × 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 h, 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 h. 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 h 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 h, 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 0.01 mm/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].

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

Neutron diffraction was used to measure phase fractions in the AM parts with a 2 mm^3 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 P4/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° and α″ for each condition. Examples of the 100% γ° 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° structure (Fig. 1f). The low impurity alloy showed 42% γ°/58% α″ in the as-built condition (Fig. 1b), which is similar to the raw powder (Fig.1 a). 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 h. 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.