Size-Dependent Microstructures in Rapidly Solidified Uranium-Niobium Powder Particles

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Abstract

The microstructures of rapidly solidified U-6wt.%Nb powder particles synthesized by centrifugal atomization were characterized using scanning electron microscopy and transmission electron microscopy. Observed variations in microstructure are related to particle sizes. All of the powder particles exhibited a two-zone microstructure. The formation of this two-zone microstructure is described by a transition from solidification controlled by internal heat flow and high solidification rate during recalescence (micro-segregation-free or partitionless growth) to solidification controlled by external heat flow with slower solidification rates (dendritic growth with solute redistribution). The extent of partitionless solidification increased with decreasing particle size due to larger undercoolings in smaller particles prior to solidification. The metastable phases that formed are related to variations in Nb concentration across the particles. The microstructures of the powders were heavily twinned.

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1. Introduction

Atomization is a widely used technique to produce rapidly solidified metal and alloy powders, as it offers a large degree of flexibility in processing combined with the potential for high levels of material production [1]. The properties of atomized powder particles can be unique due to non-equilibrium microstructural effects such as grain refinement, extension of solid solubility limits, and metastable phase formation. Uranium-niobium (U-Nb) alloys with compositions ranging from ~2–22at.%Nb (~0.8–10wt.%Nb) are known to develop various metastable phases when quenched at even relatively low cooling rates from the high-temperature γ -bcc solid solution [2-7]. Powders of these alloys could potentially be used in nuclear fuels [8], and investigations of the microstructures that form in atomized U-Nb powder particles can provide useful information for their application. As well, these types of microstructural studies are highly relevant to all rapidly solidified alloy powders produced by atomization methods.

These metastable phases that form in uranium-rich U-Nb alloys are dependent on Nb concentration, and the approximate composition ranges for the different phases have been previously determined [2-4,6,7]. Below ~15at.%Nb (~6wt.%Nb), a martensitic transformation [2-4,7] from the high-temperature γ phase produces distorted versions of the equilibrium orthorhombic α -U phase (space group Cmcm). At Nb concentrations below 9–10at.% (~3–4wt.%Nb), this distortion is manifested mainly by a contraction of the **b** axis of the unit cell as a result of Nb supersaturation, and the phase is designated α' . At Nb concentration between ~9–10 and 15at.%, the distortion is characterized by a more substantial contraction of the **b** axis accompanied by a deviation of 1–3° in the angle between the **a** and **b** axes of the unit cell to slightly greater than 90°, producing the monoclinic α'' phase. Between ~15–22at.%Nb (~6–10wt.%Nb), the γ^0 phase forms. The γ^0 phase is tetragonal with space group P4/nmn and lattice parameters $a_{\gamma^0} = \sqrt{2}a_{\gamma}$ and $c_{\gamma^0} = a_{\gamma}$. The structure is believed to arise due to correlated displacements of body-centered atoms along <100> directions of the γ -bcc solid solution [9]. The γ^0 phase

is considered to be a precursor to the α'' martensite phase [6]. Above ~22at.%Nb, sluggish kinetics [5] allow retention of the high-temperature γ phase or other metastable phases based on the γ -bcc structure.

The crystallography of the metastable martensitic phase transformations has been studied extensively [2,3,6,10-13]. The transformation is typically described by a model that produces the following lattice correspondence between the high-temperature γ phase and the α' martensite phase:

$$\begin{array}{lll} [111]_{\gamma} \rightarrow [100]_{\alpha'} & (332)_{\gamma} \rightarrow (100)_{\alpha'} & \\ [11\bar{3}]_{\gamma} \rightarrow [010]_{\alpha'} & (11\bar{2})_{\gamma} \rightarrow (010)_{\alpha'} & \\ [1\bar{1}0]_{\gamma} \rightarrow [001]_{\alpha'} & (1\bar{1}0)_{\gamma} \rightarrow (001)_{\alpha'} & \end{array}$$

The γ unit cell is transformed to the α' structure by a shear and shuffle mechanism [2,3,6,10,11]. Formation of the monoclinic α'' phase at higher solute levels results from incomplete shear due to increased lattice resistance, and increases to even higher solute levels produce even further resistance to shear, yielding the γ^0 phase [6,11]. While this model qualitatively describes the martensite transformation, experiments [13] have shown an abrupt onset of the α'' phase at a specific composition, rather than a continuous change with solute content in the degree of lattice resistance (described by the deviation from 90° in the angle γ between the **a** and **b** axes of the orthorhombic unit cell) predicted by the incomplete shear model. A twinned microstructure forms during the martensite phase transformation [6,12,14] that can be understood by considering the lattice correspondence given in equation (1). There are 12 possible orientation relationships between the high-temperature γ -bcc phase and the α -related phases (α' or α'') based on the 12 variants of the lattice correspondence. Laths or bands containing {130} or {021} twins with lath interfaces comprised of {112}, {021}, {111}, and {110} twin orientations have been predicted and observed [6,12,14].

Here, we investigate the microstructures that formed in rapidly solidified U-6wt.%Nb (~U-14at.%Nb) powders synthesized by centrifugal atomization [15,16]. Large

deviations from equilibrium are typical for rapid solidification processes such as gas atomization, resulting from large undercoolings in the molten alloy droplets and high cooling rates during solidification. As the droplet size decreases, the cooling rate will increase. However, the nucleation probability will decrease, so that the degree of undercooling also increases as the particle size becomes smaller [17,18]. Atomization yields a range of powder particle sizes, as shown in prior work on U-Nb powders [8], which implies a range of cooling rates and degrees of undercooling that give rise to a variation in powder particle microstructure. In this work, the resultant microstructures of the U-Nb powder particles were investigated as a function of particle size using scanning electron microscopy and transmission electron microscopy.

2. Experimental

2.1. Materials fabrication

U-6wt.%Nb (U-6Nb) powders were fabricated by a centrifugal atomization process [15,16] using 99% pure U and 99.8% pure Nb metal. A base pressure of 3×10^{-4} torr was obtained prior to pouring of the molten alloy. The molten alloy was supplied to the atomization chamber through a small nozzle using a feed rate ~ 50 – 100 g/s to a graphite atomization disk rotating at $\sim 30,000$ – $40,000$ rpm. The cooling medium consisted of high-purity (99.999%) Ar gas, and the atomized powder was held in the atomization chamber for 24 h in the high-purity Ar atmosphere. This allowed slow surface oxidation to passivate the particle surfaces. The mean particle size of the as-processed powder particles was 65 – 70 (± 25) μm prior to sieving the powder. The sieved powder produced two distributions, one < 50 μm with a mean particle size of 40 – 45 (± 15) and one > 50 μm with a mean particle size of 65 – 70 (± 20) μm [8]. The particle size distributions were measured with a dry particle analyzer (laser diffraction).

The average composition of the as-processed powder was measured using test method ASTM C761-04. The measured impurity levels, averaged from 2 separate measurements, are provided in Table 1.

2.2. Microstructure characterization

Specimens were prepared using an FEI Nova 600 Nanolab Dualbeam Focused Ion Beam Scanning Electron Microscope (FIB-SEM). Individual powder particles of various sizes were cross-sectioned in the FIB for analysis in the SEM. A FIB lift-out method was used to prepare specimens for the transmission electron microscope (TEM).

Secondary electron detector (SED) images were acquired in the FIB-SEM using an accelerating voltage of 5 kV. Backscattered electron detector (BSD) images were acquired using an FEI XL30S FEG SEM with an accelerating voltage of 20 kV. TEM was conducted on a Philips CM300 FEG ST TEM operating at an accelerating voltage of 300 kV. The TEM is equipped with a Gatan Imaging Filter (GIF) and an X-ray energy dispersive spectrometer (Oxford Instruments) with the INCA EDS acquisition and analysis software. Conventional TEM imaging and diffraction, annular dark-field (ADF) imaging, and energy-dispersive spectrometry (EDS) were used to analyze the particles in the TEM.

3. Results

Figure 1 presents SED and BSD SEM images acquired from cross-sectioned U-6Nb powder particles with diameters of approximately (a–c) 40, 15, and 8 μm , respectively, revealing the variation in microstructure with particle size. Dendrite formation is evident in all of the particles, and there are featureless regions of low contrast that increase in relative area fraction with decreasing particle size. This two-zone structure (a zone consisting of dendritic growth and a zone with no dendritic growth) is evident in all three of the particles. The white circle and arrow in each image of Figure 1 indicate, respectively, the approximate point of nucleation when solidification commenced and the subsequent solidification direction (the nucleation point and solidification direction are approximate due to the angle at which the particles were sectioned in the FIB). The white lines in the images represent the approximate position of the solid-liquid interface at the end of recalescence. The extent to which the two microstructural zones form,

1 clearly a function of particle size, the approximate points of nucleation, and the solid-
2 liquid interface morphology will all be addressed in more detail in the Discussion. The
3 two microstructural zones can be broadly described as dendritic and non-dendritic.

4 The higher magnification BSD SEM images in Figure 2 show the microstructure
5 variation of the dendritic zone in the (a) 40 and (b) 15 μm particles. Based on the
6 contrast in Figure 2, the dendrite features are labeled: (C) dendrite cores, (B) dendrite
7 boundary layers, and (I) interdendritic regions. These dendrite features will be referred
8 to as (C), (B), and (I) throughout. The contrast in the BSD SEM images of Figures 1 and 2
9 displays a dependence on the mean atomic number, Z [19], and indicates U-rich
10 dendrite cores surrounded by U-depleted dendrite boundary layers and an “average” U-
11 Nb composition in the interdendritic regions, as reported previously [8].

12 TEM was conducted to further assess the phases and compositions of selected
13 U-6Nb powder particles. Figure 3 presents ADF images acquired from (a) ~ 50 and (b)
14 10 μm particles. The contrast in the ADF images, while potentially exhibiting a
15 dependence on atomic number, Z [20], is largely dominated by the effects of diffraction
16 conditions, mass-thickness, and strain. The microstructural regions are evident and
17 labeled in the images, and the ADF images reveal a heavily twinned structure in the
18 interdendritic regions (I) of the dendritic zone. A banded twinned structure is evident in
19 the smaller particle shown in Figure 3(b), indicating that the non-dendritic zone (labeled
20 in Figure 3) is comprised of the same microstructure as the interdendritic regions of the
21 dendritic zone. The line across the dendrite in Figure 3(b), with labels (1), (2), and (3),
22 corresponds to the EDS spectra and line profile shown in Figure 4.

23 The three normalized EDS spectra in Figure 4(a) were extracted from the line
24 profile shown in Figure 4(b), and the points from which the individual spectra were
25 acquired are labeled (1), (2), and (3) in Figure 4 and color coded to correspond to Figure
26 3(b), showing the spatial positions of these acquisitions: (1) = (C), (2) = (B), and (3) = (I).
27 The spectra in Figure 4(a) were normalized to the maximum count value of each

individual spectrum. The normalized spectra overlap, and inspection of the figure shows a variation in the number of counts in the $\text{Nb}_{\text{L}\alpha}$ and $\text{Nb}_{\text{K}\alpha}$ peaks (~ 2.4 and 16.6 keV, respectively) that is dependent on the region of acquisition. The inset in Figure 4(a) shows the high-energy portion of the spectra for comparison of the $\text{Nb}_{\text{K}\alpha}$ peaks. The number of counts in the $\text{Nb}_{\text{K}\alpha}$ peak increases from a minimum in (C) to a maximum in (B). (Note that this trend is also evident in the $\text{Nb}_{\text{L}\alpha}$ and $\text{Nb}_{\text{K}\beta}$ peaks in Figure 4.) Figure 4(b) shows the results of the line profile analysis corresponding to the image in Figure 3(b). The dashed line with blue markers gives the wt.%Nb, as determined by the INCA software package. The Nb concentration increases from ~ 3 wt.%Nb (~ 7 at.%Nb) in the dendrite core to 8.8 wt.%Nb (~ 20 at.%Nb) in the dendrite boundary layer, then decreases to ~ 6.5 wt.%Nb (~ 15 at.%Nb) in the interdendritic region, the approximate composition of the material used to fabricate the powder. (This nominal composition of ~ 6.5 wt.%Nb was also the composition measured by EDS in the non-dendritic zone of the microstructure.) As the analysis to determine these compositions was conducted without a standard, Figure 4(b) also provides a plot of $\text{Nb}_{\text{K}\alpha}/\text{U}_{\text{L}\alpha}$ counts to illustrate more quantitatively the variation in composition (solid best-fit line with black markers). Error bars were calculated by determining the standard deviations of the $\text{U}_{\text{L}\alpha}$ and $\text{Nb}_{\text{K}\alpha}$ peaks by $\sigma = \sqrt{N}$, where N is the full-width half-maximum (FWHM) integrated intensity of each peak (number of counts) after background subtraction. This error was then propagated through to the $\text{Nb}_{\text{K}\alpha}/\text{U}_{\text{L}\alpha}$ ratio calculation. The average number of counts in the $\text{U}_{\text{L}\alpha}$ and $\text{Nb}_{\text{K}\alpha}$ peaks was, respectively, $\sim 50,000$ and $\sim 20,000$. The $\text{U}_{\text{L}\alpha}$ and $\text{Nb}_{\text{K}\alpha}$ have been determined by Romig [21] to be the optimum line combination for analysis of X-ray peaks in U-Nb alloys, as the U_{M} (~ 3.6 keV) and Nb_{L} (~ 2.4 keV) lines are of relatively low energy and limited usefulness due to absorption effects. The variation in the $\text{Nb}_{\text{K}\alpha}/\text{U}_{\text{L}\alpha}$ ratio follows the same qualitative trend as the composition measurement of the line profile, and it is evident that the ratio is lowest in (C), increases to a

1 maximum in (B), and reaches an intermediate value corresponding to the nominal alloy
2 composition in (I).

3 Figure 5 provides electron micrographs that show the microstructural regions of
4 the dendritic zone in more detail. Due to the diffraction conditions under which the ADF
5 STEM image in Figure 5(a) was acquired, dendrite cores (C) appear bright with a mottled
6 contrast, while the dendrite boundary layers (B) appear dark (the dark line surrounding
7 the dendrite cores) with an adjacent bright region that displays no contrast variation.
8 The interdendritic regions (I) appear heavily twinned, as noted previously. The ADF
9 STEM image of Figure 5(b) reveals fine-scale twinning in a dendrite core (between the
10 two black arrows, as indicated in the figure), a result of the specimen orientation
11 relative to the incident electron beam. The dendrite core consists of twinned laths that
12 are ~200–250 nm in thickness, with fine twins ~20–30 nm in thickness. This fine-scale
13 twinning is also evident in the BF TEM image of Figure 5(c) (between the white arrows,
14 as indicated). Note that this twinning is not evident in the dendrite core that spans the
15 entire image of Figure 5(c) from top to bottom, as this dendrite is not in the same
16 crystallographic orientation as the dendrite core that displays the twinning. Figure 5(c)
17 clearly shows the dendrite boundary layers, which appear bright in contrast and are
18 labeled (B) in the figure. Whether the twinning of the interdendritic region extended
19 through dendrite boundary layers was inconclusive based on the images acquired from
20 these particles, and the dendrite boundary layer may be more properly described as
21 part of the interdendritic region with an increased Nb concentration due to solute
22 rejection during dendritic solidification. Figure 5(d) provides an ADF STEM image
23 acquired from an interdendritic region, showing a twin-related lamellar domain
24 structure that is consistent with the predictions and results of Hatt [14] and Field *et al.*
25 [6], as will be discussed subsequently. The microstructure in the interdendritic regions is
26 comprised of multiple domains that contain twin-related lamellae of ~100 nm in
27 thickness.

In order to determine the phases in each of the microstructural regions of the dendritic zone and provide insight to any crystallographic relationship between phases or twin structures, selected-area diffraction patterns (SADPs) were acquired. These SADPs are provided in Figure 6. The diffraction patterns were obtained by tilting the specimen into a zone-axis orientation relative to the incident electron beam using an interdendritic region of the microstructure, then acquiring SADPs from each microstructural region in this orientation. The SADPs in Figure 6(a) and 6(b) were acquired, respectively, in the $[010]$ and $[\bar{1}31]$ zone axes of the interdendritic region (and, as seen in the figure, the dendrite boundary layer), where the zone axes and indexing of these diffraction patterns are relative to the γ -bcc phase. These orientations correspond to the $[\bar{3}12]$ and $\sim[10\bar{1}]$ zone axes of the dendrite core as labeled in Figure 6(a) and 6(b), respectively. The SADPs reveal that the phases of the (C) dendrite cores, (B) dendrite boundary layers and (I) interdendritic regions are, respectively, an α -related phase, a metastable γ -related phase, and the metastable, tetragonal γ_0 phase. The twinning in (C) is evident in the SADPs acquired from this region of the specimen. The SADPs in Figure 6 also reveal a crystallographic orientation relationship between the α -related structure of (C) and the γ -related structures of (B) and (I), given by: $(010)[101]_{\gamma} \parallel (\bar{3}12)[111]_{\alpha}$. This observed orientation relationship results in the dendrite core being slightly off of the $[10\bar{1}]$ zone axis when the interdendritic region is tilted to the $[\bar{1}31]$ zone axis, as seen in Figure 6(b). The crystallographic phases, twinning, and orientation relationship will be discussed subsequently in more detail.

4. Discussion

4.1. Solidification and Particle Microstructure

The microstructures of the rapidly solidified U-Nb particles display a clear dependence on particle size, as seen in Figure 1. The particle size affects the overall solidification time—which consists of three stages: the time to cool the superheated alloy particle to the liquidus temperature, the time associated with any undercooling, and the time

required for particle solidification and latent heat removal [22]—as particle size will influence the cooling rate, initial undercooling, nucleation temperature and rate, and crystal growth mode, all of which significantly affect the solidification microstructure. The cooling rate, $\dot{T}$, can be assessed as a function of droplet size using the expression developed by Sheng *et al.* [23]:

$$\left| \frac{dT_d}{dt} \right| = \dot{T} = \left(\frac{12}{\rho \cdot C_p} \right) (T_d - T_g) \left(\frac{k_g}{d^2} \right) \quad (1)$$

where T_d is the droplet temperature (the liquidus temperature for the exact composition U-6Nb, $T_L = 1570$ K [24] was used, which assumes no undercooling prior to solidification), ρ is the density ($\rho(T_L) = 1.6 \times 10^4$ kg/m³ [25,26]), C_p is the heat capacity ($C_p = 198$ J/(kg·K) [26]), T_g is the gas temperature (taken as room temperature, $T_g = 298$ K), k_g is the thermal conductivity of the argon gas ($k_g = 1.79 \times 10^{-2}$ W/(m·K) [23,27]), and d is the droplet diameter. Using equation (1), a plot of the cooling rate dependence on molten alloy droplet size is provided in Figure 7, with the three particle sizes shown in Figure 1 indicated on the plot. The plot shows a cooling rate of $\sim 10^6$ K/s for an 8- μ m diameter U-6Nb droplet, which decreases to $\sim 4 \times 10^5$ K/s and to $\sim 5 \times 10^4$ K/s for, respectively, 15- and 40- μ m droplets.

Measurements of the secondary dendrite arm spacing (SDAS) from the images in Figure 2 provide values of 262 ± 42 nm and 435 ± 54 nm for, respectively, the 15- and 40- μ m particles. (It should be noted that there was no secondary dendrite formation in the 8- μ m particle.) The SDAS is dependent on the particle size, with finer-scale structures forming in smaller particles, as reflected in the measurements. This particle size dependence is strongly correlated to the thermal gradient, G , and solidification rate, v , (or the local solidification time and thus the cooling rate), and the SDAS can be related to the cooling rate by [28,29]:

$$\text{SDAS} \sim \dot{T}^{-1/3} \quad (2)$$

1 The thermal gradient and solidification rate are unknown for the rapid solidification
2 process of these U-Nb particles. However, using the measured SDAS, the ratio of the
3 cooling rates for the two particles can be calculated using equation (2) and compared
4 with that of the calculated cooling rates using equation (1). The calculated ratios of the
5 cooling rates, $\dot{T}_{15\mu m}/\dot{T}_{40\mu m}$, using equations (1) and (2) are, respectively, ~ 8 and 4.5 ± 2.8 ,
6 within the same range given the error associated with measuring the SDAS and the
7 assumptions used in equation (1).

8 As stated above, the calculations using equation (1) assume no undercooling in
9 the molten droplets, using instead the liquidus temperature of the average particle
10 composition. The extent of undercooling prior to crystal nucleation is unknown in these
11 U-Nb particles, though it will be inversely dependent on the size of the liquid droplets. In
12 addition to this size dependence, the degree of accessible undercooling prior to
13 nucleation as well as the solidification behavior has been shown to depend strongly on
14 the degree of prior overheating above the liquidus temperature [30-34]. However,
15 solidification typically initiates heterogeneously on droplet surfaces during atomization
16 processes [35], as sufficiently high undercoolings for homogeneous nucleation are
17 typically not achieved unless the droplet size is extremely small [35,36]. This is largely
18 due to the size-dependent surface tension of the liquid alloy droplet, as the liquid-vapor
19 interface energy is a function of the droplet diameter when the interface is curved. It
20 has been suggested that changes to the liquid-vapor interface energy are negligible until
21 the droplet diameter is less than ~ 100 nm [37-39], though solidification rates consistent
22 with homogeneous nucleation have been observed in liquid Hg droplets with diameters
23 of 2–8 μm [40]. In the U-Nb particles shown in Figures 1 and 2, nucleation occurred at
24 the droplet surfaces based on the morphology of the solidification microstructures.
25 Given the two-zone solidification structure present in each particle (and the increase in
26 the volume fraction of the featureless, non-dendritic γ_0 regions with decreasing particle
27 size), some degree of initial undercooling was present in all of the particles prior to

1 nucleation and solidification. In the case of no undercooling, the solid-liquid interface
2 would tend toward a concentric shape (concentric isotherms as the solidification front
3 advances radially inward from the particle surface) during solidification [41], producing a
4 microstructure that varies as a function of radial position rather than a two-zone
5 microstructure across the diameter of the particle. Concentric isotherms were clearly
6 not present during solidification of the U-Nb particles.

7 When nucleation occurs in an undercooled liquid droplet, the initial solidification
8 rate can be very high and has a strong dependence on the morphology of the solid-
9 liquid interface [27] and the local composition (average impurity levels are provided in
10 Table 1). The two-zone microstructures observed in the U-Nb particles were produced
11 by the combined effects of internal heat flow and changes in temperature, velocity, and
12 morphology at the solid-liquid interface, yielding a time-dependent solidification
13 process and variation in microstructure across the solidifying droplets. The solidification
14 conditions that produce these microstructures have been analyzed in detail by Levi and
15 Mehrabian [41-43]. They showed that these two-zone microstructures result when
16 external cooling of the atomized liquid droplets is insufficient to suppress recalescence,
17 resulting in two distinct solidification modes that produce a zone that is dominated by
18 internal heat flow and high solidification rate and a zone that is dominated by external
19 heat flow and slower solidification rate.

20 When solidification commenced in the U-Nb particles (at approximately the
21 locations shown in Figure 1), the undercoolings were large enough to yield extremely
22 high solidification rates, resulting in microsegregation-free solidification in this zone. The
23 undercoolings in the particles increased with decreasing particle size, resulting in an
24 increase in the volume fraction of the non-dendritic regions that underwent
25 partitionless solidification with a composition of approximately the nominal alloy
26 composition (U-6wt.%Nb), as measured by EDS in the TEM. Based on the analyses of Levi
27 and Mehrabian [40-42], a smooth, planar solid-liquid interface traversed the particles

during partitionless solidification to produce a two-zone structure—one solid and one liquid—at the end of recalescence. The shape of this solid-liquid interface will be determined by the solidification front velocity along the interface [43]. In particles with uniform undercoolings (smaller particles), the interface will be convex toward the liquid during solidification (see Figure 1(c)), as the interface will advance in all directions from the point of nucleation at a constant rate. In larger particles with smaller undercoolings, substantial temperature gradients can exist in the molten droplets, leading to more pronounced effects of external cooling such that growth along the droplet surface advances more rapidly into a supercooled liquid while growth into the molten particle advances at a slower rate into a superheated liquid, resulting in a concave solid-liquid interface. As the particle size increases (assuming other factors such as the heat transfer coefficient remain constant), a transition between a convex to a concave solid-liquid interface (see Figure 1, where this transition from a convex to concave solid-liquid interface profile appears to occur for a particle size between 8–15 μm in these U-6wt.%Nb alloy particles) will occur, with the limit being the concentric shape discussed earlier [41] in which a molten droplet is rapidly covered by a solid shell after nucleation and solidification proceeds radially inward along concentric isotherms. After recalescence, solidification completed by latent heat removal to the particle surfaces at a considerably slower rate, yielding the segregated, dendritic structure throughout the remainder of the particles.

4.2. Metastable Phases and Twinning

The metastable crystallographic phases that formed during rapid solidification can be related to the measured compositions across the different microstructural regions in the U-Nb particles. The compositions in both the non-dendritic, microsegregation-free regions (partitionless solidification) and interdendritic regions were measured to be the approximate composition of the material (U-6wt.%Nb). The SADPs acquired from these regions (labeled (I) in Figure 6) reveal the metastable,

1 tetragonal γ^0 phase, evidenced by the weak reflections at $1/2g$ positions (these weak
2 reflections are also present in the SADPs acquired from the dendrite boundary layer,
3 particularly the $[131]$ zone axis pattern in Figure 6(b), indicating the potential presence
4 of γ_0 in region (2) as well) in the diffraction pattern, as indexed relative to the γ -bcc
5 phase, and consistent with the EDS measurements, previous X-ray diffraction (XRD) data
6 [8] acquired from these U-Nb particles, and prior studies of the composition ranges for
7 the various metastable phases in U-Nb alloys [2-4,6,7]. Given the large undercoolings
8 that likely develop in the U-Nb molten droplets, the non-dendritic regions, in which
9 solidification began, solidified at very high rates, consistent with a rapid, partitionless
10 solidification process [44-46]. The interdendritic regions of the microstructure represent
11 the last liquid to solidify in the particles, and it is evident based on the observed
12 crystallographic phase and measured composition that heat extraction was sufficiently
13 rapid during this latter stage of solidification to result in the same partitionless
14 solidification process that was active during the early stages of solidification in the
15 particles.

16 Dendrite formation is the consequence of a morphologically unstable solid-liquid
17 interface during solidification. This morphological instability is the result of solute
18 rejection from the solid as solidification progresses, leading to solute enrichment in a
19 constitutionally undercooled boundary layer ahead of the solid-liquid interface. This
20 solute rejection leads to amplification of local perturbations along the solid-liquid
21 interface and extension of these perturbations into the undercooled liquid. As the
22 undercooling-induced perturbations amplify, cusps and troughs develop and grow.
23 Solute can be rejected laterally at the peaks of the perturbations, resulting in an
24 increased undercooling and growth rate at the peaks, producing dendritic growth as the
25 solidification front advances [28]. The excess solute accumulated in the perturbation
26 troughs can lead to the formation of secondary dendrites. As shown in Figures 2–4, the
27 dendrites that formed in the U-Nb particles are comprised of a U-rich dendrite core

1 surrounded by a dendrite boundary layer that is enriched in Nb solute relative to the
2 core. This enrichment in Nb in the dendrite boundary layer was the result of Nb solute
3 rejection during dendritic growth. While it was not possible to distinguish between the
4 orthorhombic α or α' and the monoclinic α'' phases based on the SADPs (and hence the
5 patterns acquired from the dendrite core in Figure 6 are indexed relative to the
6 orthorhombic α phase), the low Nb content in the dendrite core (as measured by EDS)
7 indicates that the phase should be orthorhombic α' [2-4,6,7]. However, as the Nb
8 content in the dendrite boundary layer is much higher, there may be a gradient in
9 composition across the dendrite, potentially leading to monoclinic α'' formation in
10 regions of slightly higher Nb concentration. This could explain the contrast change at the
11 interface between the dendrite cores and boundary layers (see images in Figure 3 and 5),
12 which may be due to composition and/or strain effects. The SADPs acquired from the
13 dendrite boundary layer (labeled (B) in Figure 6) reveal extra reflections around each of
14 the Bragg reflections, predominantly in the [010] zone-axis pattern though they are also
15 present as side reflections in the [131] zone-axis pattern. The presence of these extra
16 reflections may be due to fine-scale precipitation of oxide phases, as observed in prior
17 studies [47], but could also be the result of a fine-scale composition modulation (higher
18 magnification images reveal a structure with a mottled contrast), as at elevated
19 temperatures a γ -phase miscibility gap exists in the U-Nb equilibrium phase diagram
20 [24,48] between the γ_1 and γ_2 phases at Nb concentrations higher than 17.5at.%Nb
21 (~ 7.5 wt.%Nb). The metastable $\gamma_{1,2}$ phase with intermediate Nb content between γ_1 and
22 γ_2 has also been observed to form as a precursor to equilibrium γ_2 [5,49]. In any case,
23 based on the EDS measurements (~ 8.8 wt.%Nb) and the diffraction patterns from region
24 (2) shown in Figure 6, the dendrite boundary layer is comprised of a bcc γ -related
25 structure.

26 The diffraction patterns acquired from the dendrite core (labeled (C) in Figure 6)
27 reveal the twinning of the α -related structure, also evident in the images in Figure 5(b)

and 5(c). The morphology within the dendrites consists of finely twinned laths. While a larger number of dendrite cores still need to be examined for a more in-depth analysis (twinning in the dendrite cores is the subject of ongoing studies), based on the diffraction patterns in Figure 6, these twins are consistent with a $\{130\}$ type with $\sim\{021\}$ and $\{111\}$ lath interfaces [6,10,14]. The structure of the interdendritic regions (region (I)) consist of a γ_0 martensitic twin structure, consistent with EDS measurements of the Nb concentration ($\sim 6.5\text{wt.\%Nb}$). There are multiple domains of lamellae that are twin-related about $\{110\}_\gamma$ planes, as reported in prior studies [6]. The diffraction patterns in Figure 6 confirm this type of twin structure in the γ_0 phase.

The observed crystallographic orientation relationship between the α -related structure of the dendrite core and the γ -related structures of the dendrite boundary layer and interdendritic regions, given by $(010)[101]_\gamma \parallel (\bar{3}12)[111]_\alpha$, is consistent with the following Hatt lattice correspondence [10,14]:

$$[111]_\gamma \rightarrow [100]_\alpha$$

$$(11\bar{2})_\gamma \rightarrow (010)_\alpha$$

$$(1\bar{1}0)_\gamma \rightarrow (001)_\alpha$$

Interestingly, this lattice correspondence developed in these rapidly solidified U-Nb particles during the solid-liquid transformation, similar to that observed in solid-solid transformations when U-Nb alloys were quenched from the high-temperature γ -bcc phase to the low-temperature, metastable α -related phases [6,10,14]. This orientation relationship likely developed when the interdendritic regions crystallized at the end of the rapid solidification process, with the crystallographic growth direction of the interdendritic regions (here described as both regions (B) and (I)) “templating” off of the solid dendrite cores with which the liquid was in contact.

5. Conclusions

U-6wt.%Nb powders were synthesized by centrifugal atomization and the resultant microstructures of the rapidly solidified U-Nb powder particles were investigated as a

1 function of particle size. Two microstructural zones were found to form in the particles
2 upon solidification: a non-dendritic zone that results from high solidification rate and
3 the dominance of internal heat flow during recalescence and a dendritic zone that
4 results from slower solidification rates and the dominance of external heat flow after
5 recalescence.

6 The non-dendritic zones consisted of a heavily twinned, metastable γ_0 phase
7 with the nominal composition of the alloy ($\sim$ U-6.5wt.%Nb). The dendritic zone consisted
8 of three microstructural regions with crystal structures that were dependent on the Nb
9 concentration:

- 10 • *Dendrite cores* were comprised of finely twinned laths. The measured
11 composition in the dendrite cores was $\sim$ U-3wt.%Nb. The phase was
12 determined to be an α -related structure, but it was not possible to
13 determine from electron diffraction data whether this phase was the
14 orthorhombic α or α' or the monoclinic α'' phase. Based on prior studies of
15 the composition ranges for metastable phase formation in U-Nb alloys, the
16 Nb concentration in the dendrite cores would result in formation of the
17 orthorhombic α' phase.
- 18 • *Dendrite boundary layers* consisted of a γ -related structure with a
19 composition of $\sim$ U-8.8wt.%Nb. There was no conclusive evidence for
20 twinning in these regions.
- 21 • *Interdendritic regions*, as the last liquid to solidify in the particles, consisted
22 of the same heavily twinned, metastable γ_0 phase as the non-dendritic zones,
23 with the same nominal alloy compositions ($\sim$ U-6.5wt.%Nb).

24 Twinning throughout the particles was consistent with the variants observed in prior
25 studies of U-Nb alloys, as was the lattice correspondence between the α - and γ -related
26 phases of the different microstructural regions.

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- 4

1 **Tables**

2

3 Table 1. Average impurity levels in the as-processed U-6Nb powder, measured using test
4 method ASTM C761-04. Units are in wt.% unless followed by *, which indicates ppm.

Element	Measured value $\pm$ Uncertainty
Nb	6.0 ± 0.1
Mo	0.29 ± 0.01
Ti	0.61 ± 0.02
Al	$148 \pm 1.2^*$
Fe	$54.2 \pm 0.7^*$
C	90*
O	560*

5

6

Figure Captions

Figure 1. SEM images of cross-sectioned U-6Nb particles, showing differences in microstructure as a function of particle size for particles with diameter of approximately (a) 40, (b) 15, and (c) 8 μm . The left and right columns show, respectively, secondary electron detector (SED) and backscattered electron detector (BSD) images. The white circle and arrow in each image indicate, respectively, the approximate point of nucleation when solidification commenced and the subsequent solidification direction. White lines indicate the approximate position of the solid-liquid interface at the end of recalescence. A two-zone solidification microstructure is evident.

Figure 2. Higher magnification BSD SEM images of (a) 40- and (b) 15- μm -diameter U-6Nb particles, showing the microstructural variation across the dendritic zones of the particles. The arrowed labels in the figure correspond to the different microstructural regions: (C) dendrite cores, (B) dendrite boundary layers, and (I) interdendritic regions.

Figure 3. ADF STEM images acquired from (a) ~ 50 and (b) 10 μm particles, showing the microstructural regions. The regions corresponding to the dendritic zone are labeled (C) dendrite cores, (B) dendrite boundary layers, and (I) interdendritic regions. A heavily twinned structure is evident in (I). Note the bands of this twinned structure in the non-dendritic zone at the bottom of (b), as labeled. The line with the three colored circles, labeled (1), (2), and (3) indicate the EDS line profile and corresponding spectra shown in Figure 4.

Figure 4. (a) Normalized EDS spectra obtained from regions (1), (2), and (3), acquired from the line scan as indicated in Figure 3(b). The Cu peaks are an artifact. Inset in (a) shows the high-energy portion of the spectra for comparison of the $\text{Nb}_{\text{K}\alpha}$ peaks. (b) Results of the line profile shown in Figure 3(b). The dashed line (lines are intended to guide the eye) with blue markers gives the wt.%Nb, as determined by the INCA software package. The solid line with black markers plots the ratio of the $\text{Nb}_{\text{K}\alpha}/\text{U}_{\text{L}\alpha}$ counts, with associated error. The positions labeled (1), (2), and (3) correspond to the spectra shown in Figure 3(a).

Figure 5. (a) ADF STEM image showing the different microstructural regions of the dendritic zone, with a heavily twinned interdendritic structure (I) clearly evident. (b) ADF STEM image showing fine twinning in (C) dendrite core (between arrows). (c) BF TEM image revealing the dendrite boundary layer (bright-contrast regions labeled (B)). Dendrite cores are labeled (C) for clarity, and note that the dendrite core between the white arrows shows fine twinning as in (b). (d) ADF STEM image of the interdendritic twinning (I) showing a twin-related lamellar domain structure.

Figure 6. Selected-area diffraction patterns acquired from each microstructural region of the dendritic zone, acquired in (a, b) two distinct orientations relative to the incident electron beam. Indexing of the α -related structure of the dendrite core (C) is indexed

1 relative to the orthorhombic α phase, while the γ -related structures (B,l) are with
2 respect to the γ -bcc phase.

3
4 Figure 7. Calculated cooling rate dependence on molten alloy droplet size, using
5 Equation (1). The calculation assumes no undercooling in the liquid droplet prior to
6 solidification, a droplet temperature, T_d , equal to the liquidus temperature for the exact
7 composition U-6Nb (1570 K), and thermo-physical parameters for this composition and
8 temperature: density ($\rho(T_L) = 1.6 \times 10^4 \text{ kg/m}^3$), heat capacity ($C_p = 198 \text{ J/(kg}\cdot\text{K)}$) The
9 temperature and thermal conductivity of the argon cooling gas were taken as,
10 respectively, room temperature ($T_g = 298 \text{ K}$) and $k_g = 1.79 \times 10^{-2} \text{ W/(m}\cdot\text{K)}$.
11

1 **Figures**

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