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ISOTHERMAL TRANSFORMATIONS OF URANIUM-13
ATOMIC PERCENT NIOBIUM

Ross J. Jackson

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ISOTHERMAL TRANSFORMATIONS OF URANIUM-13 ATOMIC PERCENT NIOBIUM

Ross J. Jackson

Abstract. The isothermal-transformation behavior of the gamma phase of the uranium-13 at. % niobium alloy was determined for the temperature range between 23° and 640°C. Optical and electron metallography, hardness, and X-ray diffraction techniques were used to construct a time-temperature-transformation diagram. The diagram discloses two overlapping C-curves. The upper C-curve corresponds to a lamellar precipitation of alpha plus a niobium-deficient gamma-phase which gradually enriches in niobium to form the equilibrium γ_2 structure. The lower C-curve is a general precipitation of alpha phase on dislocation.

INTRODUCTION

Two uranium-niobium equilibrium diagrams have been reported.^{1,2} The representative equilibrium phase diagram is shown by the solid lines in Figure 1. There

Figure 1. Phase relationships in the uranium-niobium system. The solid lines represent equilibrium phase relationships as determined by Rogers *et al.*,¹ and Pfeil *et al.*²

is a continuous series of solid solutions between the bcc niobium and the bcc gamma (γ) phase of uranium. The uranium-rich bcc solid solution (γ_1) at temperatures below the monotectoid-reaction isotherm (645°C) transforms diffusively into orthorhombic α (<1.0 at. % Nb) and bcc γ_2 (~72 at. % Nb). It has been reported that the γ_2 precipitate is preceded by the formation of a niobium poor bcc structure, γ_{1-2} , which is intermediate in composition to γ_1 and γ_2 . The times required to achieve equilibrium γ_2 are discussed by Ivanov and Virgiliev,³ and D. Amato *et al.*⁴ The latter reported that the initial $\alpha + \gamma_{1-2}$ precipitate is lamellar, and that the gradual decomposition of γ_{1-2} to $\alpha + \gamma_2$ is accompanied by spheroidization. Peterson *et al.*,⁵ using resistivity measurements determined the time for start of the $\gamma_1 \rightarrow \alpha + \gamma_{1-2}$ transformation in the temperature range between 450° to 550°C for times up to 100 minutes. The start-of-transformation curve was C-shaped having the nose at approximately 525°C. The nose occurred at 0-, 7-, and 11-minutes for the 5 wt % (12 at. %), 8 wt % (18 at. %), and 10 wt % (22 at. %) Nb alloys, respectively. Jackson and Miley⁶ observed the strength and structure changes on aging in the temperature range between 150° and 575°C. Their data showed a large strengthening effect at low aging temperatures (e.g., 200°C) and suggested a lower C-curve that was different in mechanism from the upper C-curve.

The isothermal decomposition behavior of the gamma phase, below its temperature range of stability, is complicated by the athermal appearance of shear-produced transition phases. The occurrence and generation of transition phases in uranium-base niobium alloys have been studied by Anagnostidis *et al.*,⁷ Tangri and Chaudhuri,⁸ and by Jackson.⁹ The transition phases, and their composition range of stability observed after water quenching from the bcc γ_1 field, are summarized as follows:

α'_a A supersaturated α -uranium transition phase containing 1 to 5 at. % Nb. The α' has the same crystal symmetry as α (orthorhombic) but differing unit cell parameters (hence the superscript). There is a notable contraction of b_0 parameter as compared to expansions of the a_0 and c_0 parameters (the subscript refers to an acicular microstructure). The α'_a probably forms via a martensitic $\beta \rightarrow \alpha$ transformation.

α_t' Similar to α_a' except for a higher niobium content (5 to 9 at. % Nb); a larger change in lattice parameters; and a highly twinned microstructure. The α_t' does not form from β , but forms via a diffusionless $\gamma \rightarrow \alpha'$ transformation.

α_t'' A supersaturated α -like transition phase containing 9 to 16 at. % Nb. The α_t'' has similar parameter changes as α' , and in addition has an increase in cell angle between the a and b axes which results in a monoclinic crystal symmetry with c axis unique. The α_t'' forms directly from γ^0 .

γ_t^0 A tetragonal transition phase containing 16 to 21 at. % Nb. The γ_t^0 is similar to the bcc γ_1 phase except two of the cell axes have expanded while the third has contracted. The structure is based on a block of $2 \times 2 \times 1$ γ -like bct subcells with $c/a < 1.0$. This results in a supercell having $c/a < 0.5$. The γ_t^0 has a twinned microstructure.

There are no major contradictions in the existing data concerning the athermal and isothermal transformations of uranium-base niobium alloys in the equilibrium $\alpha + \gamma_2$ field. However, the data are incomplete, and, at best, one could only construct partial time-temperature-transformation (TTT) diagrams. Thus, it was deemed desirable to conduct a comprehensive study of the isothermal decomposition behavior of certain uranium-base niobium alloys, from which complete TTT diagrams could be constructed.

EXPERIMENTAL

Alloy Preparation:

The uranium was magnesium-reduced material. The niobium was electron-beam-melted material rolled to 120-mil strip. The niobium averaged 40 ppm C, 5 ppm H, 50 ppm N, 80 ppm O, 10 ppm Fe, 15 ppm Mo, 10 ppm Ni, 250 ppm Ta, and 50 ppm W. The uranium averaged 10 ppm Al, 60 ppm C, 30 ppm Fe, and 30 ppm Si. The component metals were fabricated into box electrodes.

These electrodes were arc-melted in a consumable electrode arc furnace using a water-cooled copper mold. The resulting ingots were inverted and again arc-melted. The double arc-cast ingots were homogenized for 18 hours at 1100°C. The only appreciable impurity pick-up during the arc-melting and homogenization operation was an increase to about 80 ppm carbon.

Pucks were cut from the arc-cast ingots and were cross-rolled to a thickness of 90 mils. The solutionizing temperature and the intermediate annealing

temperature was 850°C. The rolling temperature varied between 850° and 550°C. This procedure resulted in a small, prior γ grain size (between 20 and 40 microns), and the grains approximated a random orientation. Disk-shaped samples, 50-mils thick by $\frac{3}{8}$ -inch diameter, were machined from the cross-rolled sheet.

Quenching and Isothermal Holding:

The samples were lightly wrapped in 2-mil tantalum sheet and encapsulated in amorphous quartz tubing under vacuum. The encapsulated samples were solutionized 30 minutes at 850°C. On quenching, pre-heated pliers were used to grasp the capsule and to plunge and crush it simultaneously into a wire basket in the low temperature bath. For the size of the samples used, the cooling rate was approximately 1000°C per sec. The samples were held in the low temperature bath for a specified time and then the wire basket and samples were quenched in ice water. The low temperature bath was either molten salt (between 450° and 650°C), liquid tin (between 250° and 450°C), or silicone oil (between 50° and 250°C).

Post-Examination Procedure:

An individual sample was used for each datum point. Each sample was examined for microstructure (by optical and electron microscopy), hardness, and crystal structure (by X-ray diffraction). For metallographic preparation, samples were subjected to one minute each on ratary laps of 180-, 320-, and 600-grit Si-C paper. Polishing consisted of one minute on 15 μ Al_2O_3 suspended in water on a no-nap cloth, then 5 minutes in a CrO_3 - $Na_2Cr_2O_7$ -water solution containing one micron Al_2O_3 on a low-nap cloth. This was followed by 18 hours on a vibratory polisher using a water slurry of 0.05 μ alumina on a low-nap cloth. The hardness values were obtained from the polished surface using a 100-gram load and are an average of at least five readings. The samples were electrolytically etched in a cold (below 10°C) 10% oxalic acid-water solution at 1.5 volts for between 10 and 60 seconds. The percent of material transformed was determined by using a point-count technique (from 200 to 600 counts) on the etched surface. Platinum-shadowed carbon replicas of the etched surface were used for high-magnification microscopy. The etched surface was also examined with filtered $CuK\alpha$ radiation from 10° to 45° 2θ at a chart speed of 1° (2 θ) per minute.

RESULTS AND DISCUSSION

Time-Temperature-Transformation (TTT) Diagram:

The TTT diagram resulting from the studies is presented in Figure 2. The solid dots represent the times and temperatures investigated. An individual sample was used for each datum point. As described in the Experimental section, the individual samples were quenched directly to the isothermal holding temperature, held for the specified length of time, and then quenched to room temperature. Each sample was examined for microstructure (by optical and electron microscopy), hardness, and crystal structure (by X-ray diffraction). The hardness results are presented in Figure 3 and representative metallographic results are shown in Figure 4. The X-ray and metallographic data, from which the TTT diagram was constructed, are listed in Table I.

The principal features of the TTT diagram are:

(a) an upper C-curve, (b) a lower C-curve, and (c) the

Figure 2. Time-Temperature-Transformation Diagram for the Uranium-13 at. % Niobium Alloy. Dots represent times and temperature studied. The (b) denotes broad X-ray diffraction lines. See text for explanation.

Figure 3. Room Temperature Hardness Values after 30 Minutes at 850°C and Isothermal Aging at the Indicated Times and Temperatures.

M_{S-f} temperatures. The M_{S-f} temperatures were determined and are discussed elsewhere.⁹ The upper and lower C-curves are discussed in the following paragraphs.

Upper C-Curve:

The equilibrium monotectoid reaction in uranium-base niobium is:

The two equilibrium low temperature phases, α and γ_2 , do not precipitate directly from the high temperature γ_1 phase, i.e., a two-stage reaction is involved. The first stage of the decomposition results in a quasi-equilibrium $\alpha + \gamma_{1-2}$ lamellar precipitate, i.e.,

The α is of near equilibrium composition while the γ_{1-2} structure is intermediate in composition to γ_1 and

(a) One minute at 600°C, single Phase α'' structure, 2100X.

(b) Ten minutes at 600°C, pearlitic $\alpha + \gamma_{1-2}$ in α'' matrix, 8000X.

(c) 10,000 minutes at 600°C, partly spheroidized pearlitic $\alpha + \gamma_2$, 100X.

(d) Ten minutes at 550°C, pearlitic $\alpha + \gamma_{1-2}$ in α'' matrix, 100X.

(e) Ten minutes at 500°C, localized pearlitic $\alpha + \gamma_{1-2}$ at some grain boundaries and inclusions, general α precipitation on dislocations, 100X.

(f) 10,000 minutes at 300°C, small amount of pearlitic $\alpha + \gamma_{1-2}$, general α precipitation on transformation dislocations, 100X.

Figure 4. Photomicrographs of Isothermally Transformed Uranium-13 at. % Niobium Alloys.

Table I. Metallographic and X-Ray Results Used for Constructing the Time-Temperature-Transformation shown in Figure 2.

Heat Treatment		Peak Width	Area Above	Phase	Percent	Hardness
Time	Temp	(112, 112)	Background	X-Ray	Pearlite	
(min.)	(°C)	(2 θ or cm)	18.5 - 19.0° θ	Ident.	Formed	(DPN)
Water quenched 850°C		1.10	0.10	α''	0	231
10 ⁵	23	1.10	0.11	α''	0	228
10 ²	100	1.10	0.10	α''	0	222
10 ³	100	1.10	0.12	α''	0	231
10 ⁴	100	1.05	0.13	α''	0	224
10 ⁵	100	1.20	0.13	α''	0	232
10	200	1.10	0.12	α''	0	224
10 ²	200	1.20	0.22	α''	0	233
10 ³	200	1.35	0.20	α''	0	262
10 ⁴	200	1.45	0.20	α''	0	274
1	300	1.15	0.15	α''	0	234
10	300	1.40	0.27	$\alpha'' + \gamma^0$ (w)*	0	288
10 ²	300	1.50	0.31	$\alpha'' + \gamma^0$ (w)	0	362
10 ³	300	2.20	0.43	α'' (b)* + γ^0 (b)	0	432
10 ⁴	300	2.25	0.49	α'' (b) + γ^0 (b)	t	525
10 sec	400	1.15	0.12	α''	0	229
1	400	1.25	0.18	α''	0	245
10	400	2.00	0.48	α'' (b) + γ^0 (b)	0	446
10 ²	400	2.20	0.42	α'' (b) + γ^0 (b)	3	523
10 ³	400	1.80	0.38	α'' (b) + γ^0 (b)	5	560
10 ⁴	400	0.55 ⁺	0.41	$\alpha + \gamma$ (3.40A)	95	461
1	450	1.10 ⁺	0.11	α''	0	232
10	450	1.40	0.22	α'' (b) veined	t	309
10 sec	500	1.00	0.09	α''	0	210
1	500	1.00	0.12	α''	5	220
10	500	1.00	0.44	$\alpha'' + \gamma$ (3.44A) + α	6	520
10 ²	500	0.70	0.42	$\alpha + \alpha'' + \gamma$ (3.14A)	31	581
10 ³	500	0.42	0.43	$\alpha + \gamma$ (3.38A)	100	479
10 ⁴	500	0.39	0.36	$\alpha + \gamma$ (3.36A)	100	364
1	550	1.20	0.12	α''	t	210
10	550	0.75 ⁺	0.36	$\alpha'' + \gamma$ (3.44A) + α	52	399
10 sec	600	1.10 ⁺	0.12	α''	0	221
1	600	1.20 ⁺	0.11	α''	0	211
10	600	1.10	0.12	α''	4	224
10 ²	600	1.15	0.20	$\alpha'' + \alpha + \gamma$ (3.42A)	6	234
10 ³	600	0.39	0.70	$\alpha + \gamma$ (3.37A)	90	348
10 ⁴	600	0.38	0.50	$\alpha + \gamma$ (3.36A)	100	334

*w denotes weak diffractions; b denotes broad diffractions.

γ_2 (~72 at. % Nb). The second stage of the transformation is the slow and gradual niobium enrichment of the $\gamma_{1,2}$ phase to equilibrium $\alpha + \gamma_2$, i.e.,

A free-energy mechanism for this sequence of transformations is shown schematically in Figure 5. The martensitic α'' phase has a lower free energy than the high temperature γ phase from which it forms. This is followed by a monotectoid decomposition to an equilibrium α structure and a nonequilibrium $\gamma_{1,2}$ structure, and a total lower free energy. The $\gamma_{1,2}$ in turn undergoes a gradual enrichment in niobium to form γ_2 plus more α , and here again a total lower free energy.

The upper C-curve represents the two-stage diffusional decomposition of γ_1 , or one of its martensitic products, to equilibrium $\alpha + \gamma_2$. The first solid line of the upper C-curve in Figure 2 represents the start of the γ_1 (or martensitic products) $\rightarrow \alpha + \gamma_{1,2}$ (α' , α'' , γ^0) reaction. The dashed line represents 50% transformed. The second solid line represents completion of the initial transformation. The third solid line represents completion of the $\gamma_{1,2} \rightarrow \alpha + \gamma_2$ transformation.

The γ_1 (α' , α'' , γ^0) $\rightarrow \alpha + \gamma_{1,2}$ upper C-curve transformation occurs via a lamellar precipitation at all temperatures and times studied. The precipitation is nucleated heterogeneously at grain boundaries and

Figure 5. Theoretical Free-Energy Diagram Showing the Sequence of Transformations Observed Experimentally.

inclusions. The lamellar structure is rarely discernible in optical micrographs, but is readily seen in electron micrographs of the properly prepared replicated surface. Figure 4 contrasts optical and electron micrographs. Electron micrographs revealed that:

- The average lamellar repeat distance, i.e., the sum of thickness of one α and one $\gamma_{1,2}$ plate, decreases with decreasing temperature of transformation. The values were 0.21, 0.12, 0.11, and 0.07 microns for 600°, 550°, 500°, and 400°C, respectively.
- The lamellar monotectoid structure, at times, degenerates into a rod-like structure. However, this structure always coexists with a predominating lamellar structure.
- In the second stage of the transformation, i.e., $\gamma_{1,2} \rightarrow \gamma_2 + \alpha$, the new alpha forms on existing alpha. A distinct secondary lamellar monotectoid reaction was not observed.
- The length-to-width ratio of the 2-D trace of the lamellar plates varied from 50:1 to 1:1; the average being ~7:1.
- The lamellar plates spheroidize, at least partially, when held for long periods of time (e.g., 10^4 minutes at 500° or 600°C) in the high temperature $\alpha + \gamma_2$ phase field.

- The equilibrium volume ratio of $\alpha:\gamma_2$ for a U-13 at. % Nb alloy was calculated to be 4.3. This calculation was based on a γ_2 composition of 51 wt % Nb^{1,2} and a unit cell value of $a_0 = 3.35 \text{ \AA}$.^{1,2,3} The measured, average-thickness ratio of the $\alpha + \gamma_{1,2}$ plates, for samples transformed at times of 10 to 10^3 minutes was 2.1. The ratios varied from 1.2 to 4.4 (any given reading was an average of at least 10 adjacent plates). Therefore, the ratio of phases (i.e., $\alpha:\gamma_{1,2}$) as first formed is verified metallographically as being a nonequilibrium ratio. X-ray diffraction studies also verified this observation. The intensity of the strong $\gamma_{1,2}$ diffraction was of near-equal intensity to the strong α diffractions. The γ diffractions were observed to decrease in intensity as $\gamma_{1,2}$ was converted to $\alpha + \gamma_2$.

Lower C-Curve:

The mechanism associated with the lower C-curve is not well understood. Experimental observations that delineate the curve are:

- The lower C-curve is characterized by an increase in hardness (Figure 3) and strength, and a change in the X-ray diffraction patterns (Table I).
- The upper portion of the lower C-curve is characterized by a general precipitation, or precipitation reaction, which occurs on transformation (twinning) or slip dislocations. Figures 4e and 4f show characteristic microstructures.
- The lower portion of the lower C-curve results in no apparent microstructural change in both optical and electron micrographs. However, shorter times are required to etch the main bands in the α'' structure.

The lower C-curve can be interpreted as a segregation reaction. Holding at the aging temperature causes one region to gradually become niobium rich while the adjacent region becomes niobium depleted. The two regions maintain coherency resulting in adjacent regions having differing cell parameters. As the composition gradient increases, the adjacent regions may have differing crystallographic symmetries while maintaining at least partial coherency. As the temperature or time of aging is increased, the degree of segregation increases such that the equilibrium alpha phase can form on dislocations. The dislocations may be transformation dislocations or slip dislocations (often polygonized). Polygonized dislocations often give rise to a veined or subgrained microstructure, whereas the transformation dislocations, especially in the early stages, cause a gradual delineation of the main bands in the α'' microstructure.

The driving force for the segregation reaction can be pictured as a metastable immiscibility gap formed by an extension of the γ_1 portions of the $\gamma_1 + \gamma_2$ and

$\alpha + \gamma_1$ solvus lines into the two phase $\alpha + \gamma_2$ phase field. The region bounded by the extrapolation of these two lines (shaded region of Figure 1) can be considered an immiscibility gap representing a $\alpha'' \rightarrow \alpha_1''$ (niobium poor) + α_2'' (niobium rich) segregation reaction. The segregation is followed by the α_1'' (niobium poor) $\rightarrow \alpha + \alpha_2''$ (niobium rich) (or $\gamma^0, \gamma_{1,2}$) transformation. If the γ_1 portion of the hypothetical $\alpha + \gamma_2$ solvus is extrapolated to intersect the immiscibility gap, a depressed monotectoid reaction results. This depressed monotectoid may be pictured as the alpha precipitation reaction.

This mechanism would account for the significant hardness increases (Figure 3) and strength increases⁶ on low temperature aging. The niobium-rich and niobium-poor regions are coherent and the motion of twinning and slip dislocation are impeded. As the aging time increases, the composition gradient increases, and the coherency strains also increase. The pre-precipitation or precipitation, of alpha on the transformation or slip dislocations, would likewise impart a strengthening effect.

The X-ray diffraction patterns after aging can be interpreted as a segregation reaction. The segregation reaction results in adjacent regions having differing cell parameters. The observed X-ray line broadening is due to a given phase having differing cell parameters and to the straining caused by the coherency requirements. As the composition gradient increases, the adjacent regions may have differing crystallographic symmetries while maintaining at

least partial coherency. This, also, causes line broadening.

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