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Phase transformation of metastable discontinuous precipitation products to equilibrium phases in U10Mo alloys

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ABSTRACT

The discontinuous precipitation (DP) mechanism is prevalent in over 80 alloy systems. We report a new type of DP occurring along prior γ-UMo grain boundaries of an alloy of uranium with 10 wt% molybdenum (U10Mo) during annealing at 500 °C, forming alternate lamellae of Mo-enriched γ-UMo and α-U. During prolonged annealing, the metastable Mo-enriched γ-UMo lamellae gradually transform into a composite mixture of equilibrium γ′-U_2Mo embedded in Mo-depleted γ-UMo. Using high resolution scanning transmission electron microscopy and atom probe tomography, a comprehensive description of the structural and compositional changes of the metastable lamellar DP product to near-equilibrium phases is provided.

Discontinuous precipitation (DP) is observed sometimes independently or in competition with a continuous precipitation (CP) mechanism in over 80 alloy systems under specific supersaturation of solute and annealing temperatures [1,2]. Modeling the competition of CP and DP mechanisms is a topic of significant fundamental research interest [2]. Such models take into account their respective influence on changing the supersaturation of solute in the parent matrix, and in determining the volume fraction of remaining untransformed parent phase, and how CP precipitates can arrest the grain boundary motion necessary for DP. In most alloy systems amenable to DP, along the grain boundaries in a solute-supersaturated parent matrix phase, alternate lamellar products form through DP, in which one phase will be the equilibrium phase with a new crystal structure, and interlamellar regions will have the same crystal structure as the parent phase but with significantly reduced solute concentration [1]. Recently, we reported a new instance of DP in a U-10 wt% Mo alloy in which the parent γ-UMo phase with about 21 at% Mo formed alternating lamellae of α-U with no Mo and Mo-enriched γ-UMo lamellae with close to 30 at% Mo [3,4]. This sets up a condition in which the metastable interlamellar Mo-enriched γ-UMo region formed by DP can then further transform into equilibrium phases, which are γ′-U_2Mo and α-U as per the phase diagram, if sufficient extent of diffusion is permitted through longer-term annealing at suitable temperatures. This new instance of DP in U10Mo alloys, and the transformation of the metastable lamellar DP product phases to near-equilibrium phases on longer-term annealing forms the subject of this publication.

Low-enriched U-10 wt% Mo alloys (hereafter referred to as U10Mo), with less than 20 wt% ^{235}U enrichment, are considered a candidate for replacing highly enriched uranium fuels currently used in all research reactors and radioisotope production facilities in the USA [5–7]. U is alloyed with 10 wt% molybdenum (Mo) to preserve the high-temperature body-centered cubic γ-U phase at room temperature in a metastable form, even under slow furnace cooling conditions [3]. Subjecting this alloy to annealing below the eutectoid temperature (~560 °C), the single-phase γ-UMo will undergo eutectoid decomposition to form α-U, which is detrimental for irradiation induced swelling of U10Mo alloys, along with γ′-U_2Mo [3,8]. Hence, there is interest in understanding the transformation mechanism and kinetics and then attempting to minimize the eutectoid transformation by additional thermomechanical treatments or by modifying the impurity concentration in the alloy. Our recent work revealed that subeutectoid annealing of U10Mo alloy at 500 °C can lead to initiation of DP (also known as cellular transformation) along prior γ-UMo grain boundaries starting from as early as 1 h, leading to formation of lamellar α-U and Mo-enriched γ-UMo in the interlamellar region instead of lamellar γ′ (U_2Mo) and α-U as predicted by the equilibrium phase diagram [3,4]. A competing CP of γ′-U_2Mo in the γ-UMo matrix also occurred after about 50 h annealing at 500 °C [3]. Complete transformation of γ-UMo in U10Mo to lamellar, discontinuous transformed regions was noted by 100 h of annealing at 500 °C [3].

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Previously, based on x-ray diffraction analysis, Repas et al. also reported the transformation of γ-UMo into α-U + Mo-rich γ-UMo lamellar microstructure through a DP mechanism, followed by an α-U + γ′ U_2Mo + γ-UMo phase mixture on longer duration isothermal annealing of U10Mo at 500 °C [9]. However, no detailed atomic-scale characterization result was provided for proving such a progressive phase transformation pathway or the spatial distribution of the product phases in the microstructure. Recently, Neogy et al. reported presence of γ′-U_2Mo in between α-U laths, where γ′ appeared to have nucleated from the α-U/γ-UMo interface, and independent γ′-U_2Mo or α-U precipitated in the γ-UMo matrix in U-9 wt% Mo alloy after long-term annealing of 5 days (120 h) and 14 days (336 h) at 500 °C [10]. However, there is still no complete understanding of the phase transformation pathway of lamellar Mo-enriched γ-UMo and α-U regions produced by DP in the early stages of annealing to the final near-equilibrium microstructure observed after many days of annealing, which is the focus of this work.

In the current work, we conduct detailed microstructural characterization of U10Mo annealed at 500 °C for 10, 50, and 100 h to understand the phase transformation pathway [11,12]. The procedure of melting, casting, and homogenization at 900 °C for 48 h, followed by subeutectoid annealing at 500 °C is described in our previous work [3]. A probe-corrected FEI 300 kV Titan scanning transmission electron microscope (STEM) was used for STEM imaging and diffraction. A CAMECA LEAP 4000× HR atom probe tomography (APT) system was used for APT analysis. The APT specimens were analyzed using pulsed ultraviolet laser (355 nm wavelength, 100 pJ laser pulse energy) while maintaining specimen temperature at 40 K and specimen evaporation at 0.005 atoms/pulse. The APT results were reconstructed using CAMECA IVAS software.

The microstructure of U10Mo homogenized at 900 °C for 48 h and subsequently annealed at 500 °C for 10 h showed signs of DP along γ-UMo grain boundaries [4]. A STEM image of the lamellar DP product along a γ-UMo grain boundary is shown in Fig. 1(a) with an inset of a selected area electron diffraction (SAED) pattern of the interlamellar γ-UMo region. The curved regions of the interface were observed to have step ledges as shown in Fig. 1(b) by red arrows. The fast Fourier transforms (FFTs) from α-U and γ-UMo lamellae are shown as an inset. A high resolution STEM (HRSTEM) image of the interface between an α-U and a γ-UMo lamella in the DP-transformed region is shown in Fig. 1(c), with a yellow arrow highlighting an extra half plane of a dislocation and a Burgers loop around the dislocation core marked with red lines. Transmission electron microscope (TEM) structural analysis revealed the orientation relationship between γ-UMo and α-U to be [100] γ-UMo||[110] α-U and {110} γ-UMo||{002} α-U. The habit plane is irrational and rotated from the {110} γ-UMo||{002} α-U plane by approximately 10° along [110]. The irrational habit plane consists of {110} γ-UMo||{002} segments and step ledges. Due to a mismatch in the lattice parameters, the γ-UMo/α-U interface is semi-coherent. The interplanar spacing of (110) planes in α-U is 2.563 Å, and that of (110) planes in γ-UMo is 2.41 Å. This corresponds to a 6.3% lattice misfit, which can be accommodated by introducing misfit dislocations every 4 nm. The atomic structure model for the interface is shown schematically in Fig. 1(d). The APT reconstruction showing the α-U and γ-UMo regions and their interface is shown in Fig. 1(e) along with the compositional profile showing the partitioning of major elements U and Mo (Fig. 1(f)) and major impurity elements (C, Al, and Si), which segregate to the γ-UMo interlamellar regions (Fig. 1(g)). Impurities appear to preferentially segregate to γ-UMo lamellae rather than α-U lamellae, based on APT analysis.

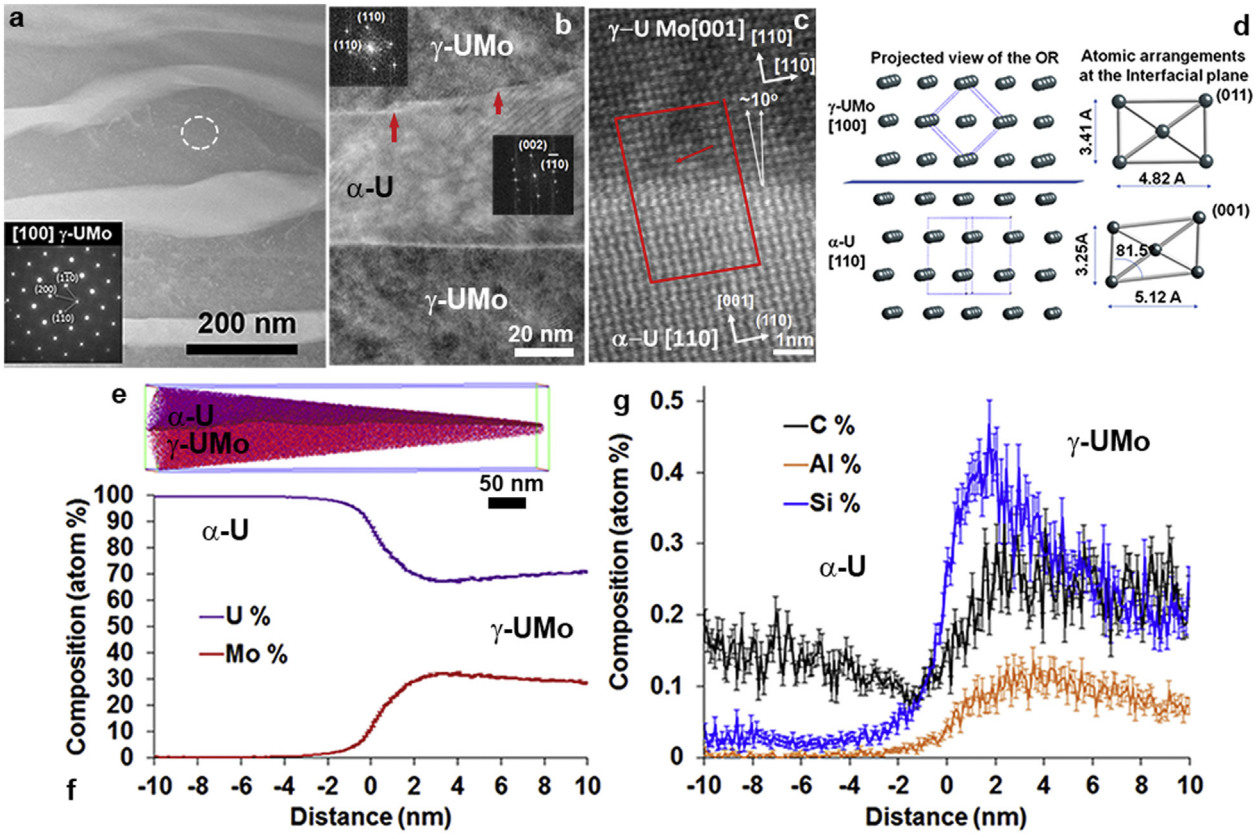

Fig. 1. a) HAADF STEM image of lamellar DP reaction product after 500 °C-10 h annealing with SAD pattern of interlamellar γ-UMo region given as inset. b) STEM image showing the presence of step ledges between α-U and γ-UMo lamellae with SAD patterns of the adjoining lamellae as insets. c) HRSTEM image of an interface between α-U and γ-UMo lamellae, revealing the orientation relationship (OR). d) Schematic representation of the OR between α-U and γ-UMo lamella. e) APT reconstruction of an interface of α-U and γ-UMo lamellae with Mo in red and U in purple. Proximity histogram across the α-U and γ-UMo lamellae interface showing compositional partitioning of f) U, Mo and g) C, Al, Si impurities. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)