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On Spinodal-like Phase Decomposition in U-50 Zr Alloy

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Abstract:

Finely dispersed two phase microstructures resulting from a spinodal decomposition are of interest as they are associated with enhanced mechanical properties and excessive interfaces to mitigate defect related behavior. This study reports a spinodal-like phase decomposition in a U-50Zr alloy by thermal annealing at 620 °C and ion irradiation at 550 °C, with the latter temperature too low to initiate phase transformation pure thermally. The results hold broad impact for U-Zr alloy systems and its application as advanced nuclear fuel.

Key words: Spinodal; Phase decomposition; Ion irradiation; Omega phase.

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The U-Zr alloy system is a promising metallic nuclear fuel for next generation fast reactors. Two of its stable phases at room temperature are α-U and UZr_{2+x}. Unlike the α-U that has been relatively well studied, many properties of UZr_2 remain sparsely reported only recently[1-4]. On the U-Zr phase diagram, there is a fairly wide composition range for UZr_{2+x}, from $UZr_{2.0}$ to $UZr_{3.2}$ with dashed boundary. Additionally, the phase boundary between the room temperature hexagonal δ-UZr_{2+x} and the high temperature bcc γ-UZr_{2+x} is a line at a temperature ~ 600 °C without a two phase co-existing region.

The phase transformation of UZr_{2+x} during cooling is relatively well understood [5]. The phase transformation from high temperature γ-UZr_{2+x} to low temperature δ-UZr_{2+x} follows a martensitic phase transformation, so called ω phase transformation, yielding a metastable transient phase precursor for δ-UZr_{2+x}, named as ω-UZr_{2+x}. The crystal structure of ω-UZr_{2+x} has basic hexagonal frame from the collapse of (111) plans of bcc γ-UZr_{2+x}, but with a lower degree of ordering on the two center atomic sites for δ-UZr_{2+x}. A followed thermal annealing of ω-UZr_{2+x} below ~ 600 °C is necessary to produce hexagonal δ-UZr_{2+x}. However, the phase transformation during heating above ~ 600 °C as well as under ion irradiation have not been explored for UZr_{2+x}.

In this paper, we used transmission electron microscopy (TEM) to in-situ follow the phase changes of hexagonal δ-$UZr_{2.6}$ to bcc γ-UZr_{2+x} during heating. We consider two cases: One where the transformation is driven thermally and one where the transformation is driven using a combination of thermal and irradiation conditions. A phase de-mixing similar to spinodal decomposition was observed for pure thermal heating up to 620 °C. A similar phase

decomposition was also observed by 1 MeV Kr ion irradiation at 550 °C at a fairly low dose. Our results suggest that the hexagonal UZr_2 phase will experience a spinodal decomposition into cubic γ phase under thermal irradiation conditions. This observation is important for U-Zr based alloys and nuclear fuel because the cubic phase is associated with isotropic dimensional changes under irradiation and as a consequence will exhibit smaller swelling rates than the hexagonal phase.

An alloy rod was prepared by arc melting depleted U metal and Zr blocks at a composition of U-50 wt.% Zr, yielding a chemical stoichiometry of $UZr_{2.6}$. The rod was naturally cooled down to room temperature, then thermally annealed at 550 °C for 24 hours. All experiments were conducted inside an argon glovebox with O_2 less than 10 ppm. TEM samples were prepared by focused ion beam (FIB) lift-out method using a Quanta 3D system at Irradiated Materials Characterization Laboratory (IMCL) at Idaho National Laboratory. In-situ thermal treatment and ion irradiation experiments were conducted in the Intermediate Voltage Electron Microscope at Argonne National Laboratory. A Gatan heating stage was used to heat the TEM FIB sample during the in-situ irradiation study using 1 MeV Kr ion irradiation. The TEM sample thickness and radiation damage and implanted ion deposition from Kr ions are laid out in Figure 1, showing that the dominant irradiation effect in the UZr_2 TEM sample is defect generation rather than ion implantation. Damage profile and Kr ion distribution was simulated by SIRM 2013 using Kinchin-Pease model. 61 eV [6] and 35 eV [7] were chosen as the atom displacement energy for uranium and zirconium atoms, respectively. An incidence angle of 15° was used for the SRIM damage calculation. This angle is the one between ion beam and the normal direction

of TEM FIB lamella. After ion irradiation, detailed microstructural characterization of the irradiated samples was carried out using a FEI Talos 200 FX STEM at IMCL.

A detailed phase identification is essential for a pre-irradiation experiment. The casting process involves cooling of UZr_{2+x} solution from a liquid to a solid state and eventually crossing the solid phase transformation line at ~ 610 °C. For the ω phase transformation from bcc to hexagonal, there are two steps [8, 9]. The first step involves a rapid diffusionless collapse of (111) lattice plane from the bcc phase, constructing the hexagonal crystal structure frame from the parent bcc crystal structure. The second step involves sluggish thermal aging that introduces "ordering" for the occupancy of atomic sites. In this study, the relatively fast cooling rate during cast hindered the chemical ordering part of the ω phase transformation but allows $UZr_{2.6}$ to obtain a basic hexagonal structure. Subsequently, the cast pin was thermally annealed for 24 hours at 550 °C. The aim of the this step was to introduce ordering of the atomic occupancy by U and Zr inside the primitive hexagonal structure through a process referred to as "chemical partial ordering (CPO)"[5].

The XRD spectrum for $UZr_{2.6}$ is shown in Figure 2, along with the theoretical spectra for bcc-$UZr_{2.0}$ and hexagonal-$UZr_{2.0}$, with and without CPO. The XRD spectrum of the annealed sample exhibits different features from bcc-$UZr_{2.0}$ but is similar to hexagonal-$UZr_{2.0}$, indicating that the crystal structure has hexagonal symmetry and the first step of the ω phase transformation is complete. However, the peak intensities are substantially different. Compared to the theoretical spectrum, the experimental peaks at $(11\bar{2}0)$ and $(22\bar{4}0)$ have a much higher intensity relative to other peaks. Those two peaks overlap with (011) and (022) peaks for bcc- $UZr_{2.0}$. This match

indicates the crystallographic coherency between the bcc and hexagonal structures. In fact, researchers are proposing that the delta phase is developed inside the bcc parent grains through the ω phase transformation [5]. Zoom in region on XRD spectrum shows the degree of CPO of hexagonal-UZr_2 phase. Those peaks for annealed sample are very weak, suggesting the sample did not achieve CPO. In other words, the second step (i.e. the diffusion component) of the ω phase transformation was not completed.

TEM selected area electron diffraction (SAED) patterns provide more direct evidence concerning the completion of the ω phase transformation. In a similar system, the Zr-Nb alloy [8], lines of intensity and weak streaks between bright diffraction spot indicate a lower degree of chemical ordering of ω phase. In a separate study, solution-treated Ti-Al-Nb alloys were cooled down by different methods, ranging from water quenching, air cooling, to furnace cooling. Consequentially, SAED patterns changed from weak streaks, to tweed-like contrasts, to bright convergent spots, respectively, indicating a gradually increased degree of CPO [10]. Similarly, we observed tweed-like contrasts on SAED patterns (with two shown in Figure 2 b and c), indicating the diffusion component of the phase transformation from bcc-$UZr_{2.6}$ to δ-$UZr_{2.6}$ was ongoing but not completed. Based on the XRD and TEM results, the samples will hereafter be referred to as ω-$UZr_{2.6}$ instead of δ-$UZr_{2.6}$.

An in-situ heating of ω-$UZr_{2.6}$ was conducted inside a TEM. The starting microstructure contained band contours viewed along the $[01\bar{1}0]$ zone axis of the hexagonal crystal structure (Figure 3, a-c). During heating, the clean microstructure changed into apparently intertwined dual phase right after the temperature passed 610 °C. The temperature was then deliberately

stabilized at 620 °C for microstructure characterization. During this period, the microstructure evolved into an apparent dual phase structure (Figure 3, d-e). Multiple satellite spots appeared around the major spots in the SAED patterns which is indexed as the [111] zone of a cubic phase (Figure 3, f). After isothermally holding at this temperature for 0.5 hour, the sample was cooled to room temperature using a relatively slow cooling of 50 °C/ min. The dual phase feature was successfully preserved down to room temperature (Figure 3, g-h). The satellite spots converged and the SAED pattern is indexed as bcc [111] zone (Figure 3 i).

The STEM EDS indicates the dual phase microstructure is a mixture of Zr and U rich phase (Figure 3, j-i). For the region enriched by Zr, the composition reached a plateau across a length of 30-40 nm. The Zr-lean phase, on the other hand, has a smaller width ~ 10 nm. Based on EDS line scanning over at least five regions for each type, the chemical composition is found to be $U_{15\pm4}Zr_{86\pm5}$ for Zr rich regions and $U_{61\pm3}Zr_{40\pm2}$ for U rich regions. Furthermore, the dual phase encompasses the entire TEM lamella, did not show denuded zone along grain boundary as shown in Figure 3 g at the region highlighted by red dashed line same as in Figure 3a, Similar phenomena has been observed previously for thermally annealed Fe-Mn-Al-C austenitic alloys, and attributed to spinodal decomposition [11]. In fact, such an omnipresent feature is one of the major differences between spinodal decomposition and nucleation and growth of new precipitates in an existing solid matrix [12].

During the phase transformation, SAED pattern changed from clear bright dots for ω-$UZr_{2.6}$ (Figure 3c) to clustering of satellites spots around the major dots for bcc γ-$UZr_{2.6}$ at 620 °C (Figure 3f) and was preserved to room temperature (Figure 3i). Although a phase change form

hexagonal to cubic is expected at 620 °C, the emergence of dual phase of cubic structure is not envisioned. The clustering of diffraction dots for cubic phase indicating the newly formed phase shares crystal structure with slightly different lattice parameter. Should this phenomenon be followed by XRD, it will show up as sideband along the main peak of (110) planes as observed before for spinodal decomposed phases [13]. The current SAED data does not contain enough information to distinguish between bcc and fcc phases but from previous data it is assumed that the cubic phase has a bcc structure. In fact, being of the same crystal structure between the parent phase and decomposed phase is another feature of spinodal phase decomposition[13]. Since the newly formed phases are of cubic symmetry, it is reasonable to expect the ω-$UZr_{2.6}$ firstly converted to cubic symmetry and then went through the spinodal phase decomposition to phases of different composition but same crystal symmetry.

Both chemical and phase information indicates the observed phase transformation is a spinodal like phase decomposition process. It is a de-mix of a single phase into two phases that share coherency of crystal structure but with dramatic difference of chemical composition. Unlike nucleation that requires to pass a large energy barrier, spinodal phase decomposition occurs spontaneously when the single-phase solid solution is annealed at temperatures fall in a "miscibility gap". It is a phase de-mix process whose nucleation does not relies on pre-existing extended defect structure, such as dislocation lines, and grain boundary. For this reason, the spinodal phase mixtures occupied the whole structure without appreciable difference between grain boundary areas and interior regions. However, such a miscibility gap is not shown on the U-Zr phase diagram, although a previous study mentioned there is a two-phase region of δ and bcc for a narrow temperature range of 5 °C around 610 °C at compositions of 63-82 at. % Zr

[14]. How high the temperature can be on the dome point of this miscibility gap remains an open question for now and worthy further study.

It is notable that this is the first time a spinodal decomposition is experimentally observed for U-Zr although it has been reported for other alloy systems, such as Fe-Ni[15], Ag-Cu[16], and W-Re[17]. It is an important phenomenon that can lead to significant changes in the physical properties of U-Zr alloys. In fact, the spinodal decomposition has been shown to be an effective way to produce materials with nanosized domains and excessive amount of surface to improve the strength of alloys by blocking dislocation movement. For instance, through tuning of Al concentration, a 200 nm interconnected spinodal structure can be created in $Al_{0.9}CoCrFeNi$ high entropy alloys and produces a remarkably high hardness [18]. Another study on spinodal phase breakdown of Fe-Ni-Cr to FeNi and Fe_3Ni indicates it may be responsible for the loss of resistance to void swelling [19]. The spinodal structure found in this study for ω-$UZr_{2.6}$ indicates a hardening could occur for U-Zr based nuclear fuel considering the amount of UZr_2 phase present. How its influences on metallic fuel performance are unknown and worthy of further study.

A similar behavior was observed for ω-$UZr_{2.6}$ under 1 MeV Kr ion irradiation at 550 °C (Figure 4). At a dose of 0.2 displacements per atom (dpa), the microstructure changes into a phase mixture similar to the thermal treatment induced microstructure shown in Figure 3. The size of the new de-mixed phase increases with radiation dose (Figure 4c). Correspondingly, the tweed-like contrasts (highlighted by red arrow) in Figure 4d vanished at 0.2 dpa (Figure 4e and f). Instead, the major diffraction spots along the bcc [111] direction have been divided into multiple

weaker spots. Those satellite spots clustered around the prior points similar to Figure 3f and 3i. STEM EDS (Figure 4 g-i) shows similar fluctuations of U and Zr concentration throughout the sample. However, the composition profiles (Figure 4 i) have sharp spikes instead of plateaus, as shown in Figure 3i.

Spinodal decomposition of model alloys begins with the instability of an infinite isotropic solid with respect to long-range infinitesimal compositional fluctuations. The underlying driving force is the supersaturation of point defects [20] in a destabilized solid solution. It can be well explained by inverse Kirkendall effect [21]. Both thermal annealing at high temperature and irradiation can create a solid solution with saturated concentration of point defects, including vacancies and interstitials. The combination of interstitials with vacancy can be element dependent, creating a back diffusion of displacement of one spice at the sacrifice of the other and resulting composition modulation as observed here. In our study, the 1 MeV Kr ions successfully trigger the spinodal-like decomposition of ω-$UZr_{2.6}$ even at 550 °C, a stable temperature for ω-$UZr_{2.6}$ under isothermal conditions. Without irradiation, this ω-$UZr_{2.6}$ is expected to achieve CPO and become δ-$UZr_{2.6}$, unlike the de-mixed phase being observed in this study. Noteworthy, this irradiation temperature is also the fuel periphery temperature for U-Zr based metallic fuel, the observed spinodal-like phase decomposition could possibly be the very beginning of the observed phase decomposition found numerously in post irradiation examination of U-Zr based metallic fuel [22].

In Summary, for the first time, a thermal annealing-induced spinodal-like phase decomposition is observed at ~620 °C in a U-50Zr alloy upon heating just above the ω phase transition temperature. The decomposed phase mixtures are around 50 nm in size and have same cubic

crystal structure but of large fluctuation of chemical compositions. A similar phenomenon is observed for the same alloy irradiated by 1 MeV Kr ion at 550 °C, a temperature below the phase transformation, and was attributed to inverse Kirkendall effect. Ion irradiation creates a supersaturation of point defects, which destabilizes the alloy system and induces a spinodal-like phase decomposition at temperatures lower than expected for thermally induced decomposition. The observed nanosized spinodal phase have the potential to harden the materials and reduce void swelling. Both are encouraging behaviors for its application as advanced metallic nuclear fuel and worthy of further investigation.

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Figure Captions

Figure.1 (Color online) Overlay of TEM sample (dark gray box) with radiation damage (orange curve) by 1 MeV Kr ion beam and its distribution (blue curve) at a fluence of 1E15 ions/cm^2. UZr_2 phase region of U-Zr system was also inserted with different UZr_2 phases and transformation temperatures highlighted. Readers are referred to online color vision.

Figure 2 (Color online) (a) XRD spectrum of $UZr_{2.6}$ pin after thermal annealing at 550 °C for 24 hours, showing the crystal structure is hexagonal but with limited ordering as indicated by the weak peak for CPO at 20.36° and absent at other 2θ positions; (b) and (c) show the faint streaks beside the major spots on SAED, indicating that the ω phase transformation is still ”on going”. Readers are referred to online color vision.

Figure 3 (Color online) TEM bright field images and SAED for sample at room temperature (a-c), at 620 °C (b-f), and cooled to room temperature after being held at 620 °C for 30 min (g-i), STEM-EDS mapping obtained at room temperature showing spinodal like phase decomposition (k-i). Readers are referred to online color vision.

Figure 4 (Color online) TEM and corresponding SAED for samples irradiated at 550 °C by 1 MeV Kr (a, d) to 0.2 dpa (b, e) and 1.3 dpa (c, f). STEM-EDS analysis shows the obtained microstructure is similar with the microstructure obtained after thermally heating the sample to 620 °C as shown in Figure 3. Readers are referred to online color vision.