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Micro-structural study and Rietveld analysis of fast reactor fuels: U–Mo fuels

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HIGHLIGHTS

- U–Mo alloys in as-cast as well as in annealed conditions have been studied using Optical Microscope, SEM, XRD.
- The monoclinic α'' phase in as-cast U-10 at.% Mo alloy has been characterized through Rietveld analysis.
- The dendritic microstructure of γ-(U,Mo) and B.C.C. 'Mo' phase of 33 at.% U–Mo alloy have been analysed.
- Rietveld analysis has been done to optimize lattice parameters and calculate phase fractions in annealed alloys.
- The Vickers microhardness of U_2Mo phase shows lower hardness than two phase microstructures in annealed alloys.

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ABSTRACT

U–Mo alloys are the candidate fuels for both research reactors and fast breeder reactors. In-reactor performance of the fuel depends on the microstructural stability and thermal properties of the fuel. To improve the fuel performance, alloying elements viz. Zr, Mo, Nb, Ti and fissium are added in the fuel. The first reactor fuels are normally prepared by injection casting. The objective of this work is to compare microstructure, phase-fields and hardness of as-cast four different U–Mo alloy (2, 5, 10 and 33 at.% Mo) fuels with the equilibrium microstructure of the alloys. Scanning electron microscope with energy dispersive spectrometer and optical microscope have been used to characterize the morphology of the as-cast and annealed alloys. The monoclinic α'' phase in as-cast U-10 at.% Mo alloy has been characterized through Rietveld analysis. A comparison of metallographic and Rietveld analysis of as-cast (dendritic microstructure) and annealed U-33 at.% Mo alloy, corresponding to intermetallic compound, has been reported here for the first time. This study will provide in depth understanding of microstructural and phase evolution of U–Mo alloys as fast reactor fuel.

1. Introduction

The U–Mo alloy had been used as fuel for early metallic fuel fast reactors viz. Enrico Fermi Reactor (Fermi-I) in USA. A significant number of metallic fuel rods of U–Zr, U-fissium and U–Zr-X have been burnt in EBR and FFTF [1]. There are several experimental, pilot and demonstration fast breeder reactors; e.g. FBTR (India), DFR (UK), RAPSODIE (France), JOYO (Japan), PFR (Germany) and BOR-60 (Russian federation), BN600 and Super-phenix (France) [2]. The world over people has opted for more technologically mature, oxide fuel option. The rationales for extensive usage of oxide fuels are of ease of fabrication, handling and reprocessing. However, with the advancement of technology, it is now feasible to conveniently fabricate, handle and reprocess metallic fuels. The main advantages of metallic fuels over conventional ceramic fuels are high breeding ratio, high thermal conductivity and better in-reactor behavior during transient conditions. The economic competence of metallic fuel driven fast breeder reactor depends on high burn–up of metallic fuels. Though currently India is in a process of commissioning Prototype Fast Breeder Reactor (PFBR), fueled by conventional $(U,Pu)O_2$ – MOX fuel, but upcoming FBRs are planned to be fueled by uranium based metallic alloys.

Pure uranium has three stable allotropic phases, orthorhombic α-U (−231 °C–667.3 °C, 4 atoms/cell), tetragonal β-U

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(667.3 °C–774.8 °C, 30 atoms/cell) [3] and body-centered cubic γ-U (774.8 °C–1135 °C, 2 atoms/cell). Other than BCC γ-U, all allotropes of uranium, orthorhombic (α-U) and tetragonal (β-U), show anisotropic expansion coefficients. Alloying of 'U' fuel with some transition group elements e.g., Zr, Mo, Nb, Ti and fissium is highly desirable as these elements can raise the fuel solidus temperature and stabilize BCC γ-U phase to lower temperature, thus enhancing its dimensional stability. These alloying elements also facilitate in improving the structural integrity of the fuel under irradiation and lower the fuel-clad chemical interaction. Molybdenum has a BCC crystal structure up to its melting point, at 2450 °C. It has high thermal conductivity (138 W/m/K compared with Zr 22.6 W/m/K) and can be added to stabilize the BCC γ-U phase over a wider temperature range, while maintaining a high uranium density. 'Mo' has reasonable solubility in BCC uranium to form an alloy of γ-(U,Mo), that shows isotropic expansion with increase in temperature. The orthorhombic α-U and tetragonal β-U show negligible solubility of molybdenum, thus they do not get stabilized by addition of 'Mo'.

As seen from Table 1, many researchers [4–24] have carried out metallographic investigations of U–Mo system. Tangri and Williams [10] investigated U–Mo alloys, with 0.67–11.39 at.% Mo, under three different heat treatment conditions: water quenched (~1000 °C/sec), argon quenched (~220 °C/sec) and air cooled (~10 °C/sec), from below solidus temperature. In U–Mo alloys with less than 2.95 at.% Mo, they observed α′, β, β+α and β+α′, depending on 'Mo' concentration. In case of alloys with 2.95–6.2 at.% Mo, all water quenched samples were reported as α′-U (distorted orthorhombic). As expected, they observed that water-quenched alloys showed 'b' parameter contractions, while lattice parameter 'a' and 'c' remained almost constant, with increase in 'Mo' content. Alloys with low 'Mo' content (≤6.2 at.%) undergo transition from γ-U to α′-U (distorted orthorhombic) on water-quenching, whereas, alloy with 7.2–~11.18 at.% 'Mo' forms α''-U (monoclinic) on water-quenching. Stewart and Williams [16] have reported appearance of monoclinic structure (α″) even in the alloy with 5.9 at.% Mo, in water quenched sample. They observed α″-U monoclinic in water quenched alloy with 5.9–11.2 at.% Mo. However, they have made an observation that the water-quenched alloys in the composition range 5–7 at.% Mo tend to reach the lattice parameter and angle limit from monoclinic (α″-U) to distorted orthorhombic (α′-U). This small difference in composition limit for BCC → monoclinic vs BCC→distorted orthorhombic between the two reported works, 6.2 at.% Mo [10] and 5.9 at.% Mo [16] may be associated with slight difference in quenching process. With decrease in 'Mo' content, γ-angle approached 90°, thus distorted orthorhombic (α′) is the lower limit of monoclinic (α″) deformation. Hence, the switch from monoclinic (α″) to orthorhombic (α′) may be between 5 and 7 at.% Mo. Lehmann [7] and Lehman and Hills [8] also reported appearance of monoclinic (α″) phase in alloys with 4.6–9.4 at.% Mo, after oil-quenching from 950 °C. Using dilatometric method, Howlett [13] investigated phase transitions in U–Mo alloys with 6.0–12.5 at.% Mo. He carried out ice-brine quenching (~50 °C/sec) and air-quenching from 700 °C (~2.3 °C/sec). He could not establish whether U–Mo alloys with 6–8% Mo had α′ or α″ structure, because the angle was very close to 90°. However, for alloys with >8% Mo, he found (α″) phase for both air and ice-brine quenching. Stewart and Williams [16] reported formation of α″ from γ_d' for alloys with 9.2–10.8 at.% Mo. γ_d' is an intermediate tetragonal structure formed before bcc-γ phase while heating room-temperature alloy with metastable α″ structure. According to them the transition from high temperature, γ_d'-tetragonal to low temperature α″-monoclinic is a reversible transition. Ostberg et al. [14] have investigated isothermal phase transitions of U-3.88 at.% Mo. They annealed the alloy at 950 °C under vacuum and then held them at 640 °C, 600 °C, 550 °C, 525 °C and 500 °C, then quenched in Pb–Sn quenching bath.

However, most of these researchers were interested in investigating the properties of U–Mo plate-fuel. Plate fuels operate at low temperature (peak fuel centre-line temperature 250 °C) [19] and

Table 1
Literature data on metallurgical investigations of U–Mo alloy along with their compositions and type of heat treatments.

At.% Mo	Heat treatment/Processing	Analysis	Hardness	Ref.
12.40–25.27	Water quenched from 1000 °C and isothermally transformed into 570 °C to 200 °C	LM[a] and XRD	Yes	[4]
5–10	Hg quench from 900 °C	LM, XRD	NA	[5]
1.96–36.78	Annealed at different temperatures and water quenched	LM,XRD, Chemical analysis	NA	[6]
0–30	Annealed at 950 °C and 1000 °C and 'Hg', or oil quenched	LM,XRD	NA	[7,8]
2.5–15	Hg quenched from 1000 °C	LM and XRD	Yes	[9]
0.67–11.39	Annealing at 950 °C with water& Ar quenching and air cooling	LM, XRD	NA	[10]
0.49–4.82	Annealing at 950 °C or 800 °C then slow cooling, step, water quenching or furnace cooling to room temperature.	LM,SEM, XRD	NA	[11]
6–12.5	Annealing at 950 °C and water quenched	Dilatometry, LM and XRD	NA	[12,13]
3.88	Annealed at 940 °C and isothermal between 500 and 640 °C	LM, SEM and XRD	NA	[14]
7.12–25.28	Annealed above 800 °C and quenched to transformation temperature	LM,XRD	Yes	[15]
5.9–10	Annealed at 940 °C and water quenched	XRD	NA	[16]
0	As-cast; 625 °C for 8 h & vacuum cooling	LM, XRD	Yes	[17]
3.64	As-cast, Annealed; As-rolled at 625 °C and 800 °C; Rolled at 600 °C & 800 °C and γ-quenched from 800 to 850 °C		Yes	
9.36–21.60	As-cast alloy annealed in 900 °C and air-cooled and irradiation	LM and XRD	NA	[18,19]
6–12	Annealing at 900 °C and slow cooling, Annealing at 850 °C and quenched in water, oil or sand and cooled in flowing He	XRD	NA	[20]
15.73–25.28	Hot rolling at 650 °C	LM, XRD	NA	[21]
0–15	Splat cooling	SEM, EBSD[b] and XRD	NA	[22]
11–17	Splat cooling	XRD	NA	[23]
11.55, 15.73, 21.61	As-cast Annealed 300 °C for 72 h & 240 h. Annealed at 500 °C for 72 & 240 h.	LM, FE-SEM[c], AFM[d], EFM[e] and XRD	Yes	[24]

[a] LM: Light microscope.
[b] EBSD: Electron backscatter diffraction.
[c] FE-SEM: Field emission scanning electron microscope.
[d] AFM: Atomic force microscope.
[e] EFM: Electrostatic force microscope.